# Software for Chemical Engineering Thermodynamics

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by

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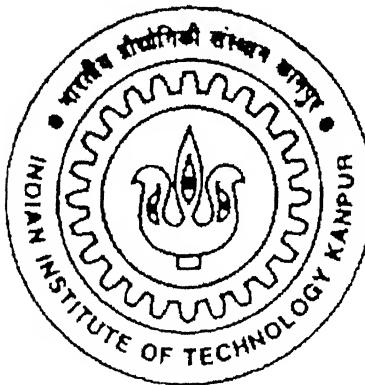
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Certificate

This is to certify that the work contained in the thesis entitled "**SOFTWARE FOR CHEMICAL ENGINEERING THERMODYNAMICS**" has been carried out by *Hasanat Ahmad Khan* under my supervision and that it has not been submitted elsewhere for a degree.

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Abstract

A knowledge of thermodynamic properties is of immense importance for the design and development of processes and equipment. In several situations in which no experimental data for the necessary properties is at hand, the values must be predicted. The work reported in this thesis is an attempt to develop a computer software to estimate thermodynamic properties of importance in chemical engineering, using cubic equation of state. The cubic equations of state used for the estimation of properties are *van der Waals equation, Redlich Kwong equation, Soave Redlich Kwong equation* and *Peng Robinson equation*. The software includes programs for predicting properties for pure components as well as multi-component mixtures. For pure substances the properties included are *molar volume, departure functions, fugacity, saturation pressure, saturation temperature, vapor enthalpy* and *vapor entropy*. For multi-component mixtures, it includes *molar volume, departure function, fugacity* and *partial fugacity*. In addition to performing the *phase equilibrium calculations* the software is also capable of predicting *vapor-liquid equilibrium data (VLE)*. For the VLE data prediction it uses five different activity coefficient models including *UNIFAC*. The software also contains an inbuilt database, which includes 250 compounds.

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List of Symbols

A	Margules parameter
A	Van Laar parameter
a	Parameter in Equation of state
a_{mn}	UNIFAC group interaction parameter
B	Van Laar parameter
dh	Enthalpy departure
ds	Entropy departure
f	Fugacity
G_{ij}	NRTL parameter
g^E	Excess Gibbs free energy
h	Enthalpy
K_i	Equilibrium Constant
P	Pressure
Q_k	Group area parameter
R	Universal gas constant
R_k	Group volume parameter
s	Entropy
T	Temperature
u_{mn}	Measure of interaction energy between groups m and n
V	Volume
$V_{i,j}$	Wilson parameter
v	Molar volume
x_i	Mole faction of component i in liquid phase
y_i	Mole fraction of component i in vapor phase
Z	Compressibility factor

Greek letters

α	Temperature dependence of parameter a
Γ_k	Group residual activity coefficient
$\Gamma_k^{(i)}$	Residual activity coefficient of group k in a reference solution containing molecular species i
γ	Activity coefficient
θ_i	Area fraction of component i
θ_m	Surface area fraction of group m
v_k^i	Number of groups type in a molecule of component i
ϕ	Fugacity coefficient
$\hat{\phi}_i$	Fugacity coefficient of component i in mixture
ω	Acentric factor

Superscripts

l	Liquid phase
o	Reference state
v	Vapor phase
s, Sat	Saturated

Subscripts

c	Critical property
i,j	Molecular species
k	Subgroups
m	mixtures
r	Residual property

Chapter 1

INTRODUCTION

The main activities of a chemical engineer are concerned with the design and development of new processes or the improvement of existing processes for converting the raw materials into useful products of greater value in an optimal way. The resources available to an engineer are the raw materials, space and time. The emphasis should be given on consuming minimum amount of resources for producing the desired products. But before initiating the task one should know its viability, the energy requirement and the fractional conversion of the raw materials into product, for the process. For example, designing a process for producing alcohol by a specific reaction requires the knowledge of the feasibility of the reaction at a particular temperature and pressure, the extent to which the reaction can proceed, the energy requirement for the reaction, the effect of change in operating condition and energy required to separate the desired product from the byproducts and the reactants. All these information can be obtained by the application of the principles of thermodynamics.

In thermodynamic analysis of a process, it is essential to have knowledge of the properties of the system and the relationships that exist among the various properties. The properties of interest in thermodynamics can be broadly classified into two groups as

> ➤ Measurable Properties and
> ➤ Non-measurable Properties.

The properties which can be directly measured, like pressure (P), temperature (T) and Volume (V), are called measurable properties and the properties, that cannot be directly measured, like internal energy (U), enthalpy (H), Helmholtz free energy (A), entropy (S), Gibbs free energy (G), etc., are called non-measurable properties. The properties are independent of the path followed by a system in reaching a given state as the change in the properties depends only on the initial and the final state of the system. As a property has a unique value when a system is in a given state, the non-measurable properties can be estimated in terms of the measurable properties, T, v and P. There

exist fundamental property relations, which contain all the information about the system and if they are known, in principle, each and every property of the system can be estimated. There are several alternative fundamental relations. The most commonly used fundamental relations are

$$U = U\ (S,\ V,\ N_1,\ N_2,\ N_3,\ ...,\ N_n) \tag{1.1}$$

$$H = H\ (S,\ P,\ N_1,\ N_2,\ N_3,\ ...\ ,\ N_n) \tag{1.2}$$

$$A = A\ (T,\ V,\ N_1,\ N_2,\ N_3,\ ...,,\ N_n) \tag{1.3}$$

$$G = G\ (T,\ P,\ N_1,\ N_2,\ N_3,\ ...,,N_n) \tag{1.4}$$

$$S = S\ (U,\ V,\ N_1,\ N_2,\ N_3,\ ...,\ N_n) \tag{1.5}$$

Where,

N_n is the number of moles of the component n in the system.

The first relation is the fundamental relation in the energy representation and the next three are the partial Legendre transforms of the first relation. The last relation is the fundamental relation in the entropy representation. First four relations are called thermodynamic potentials and they can be effectively used for developing the relationships among the thermodynamic properties. For a simple compressible system H, S and V can be written as a function of T and P as

$$H = H\ (T,\ P), \tag{1.6}$$

$$S\ =\ S\ (T,\ P) \tag{1.7}$$

and $\qquad V = V\ (T,\ P) \tag{1.8}$

If H, S and V are known for a particular system, then, G, U and A can be calculated from the following relations

$$G = H - TS \tag{1.9}$$

$$U = H - PV \tag{1.10}$$

$$A = U - TS \tag{1.11}$$

Usually, the thermodynamic property data is presented in the following three forms

> ➢ Equation Of State (EOS),
> ➢ Diagrams and charts and
> ➢ Thermodynamic property tables.

The EOS are the relationships between P, v and T, having the form $f(P, v, T) = 0$, and are valid over a wide range of temperature and pressure. Several forms of EOS are available and they are discussed in *Chapter 2*. There are several thermodynamic charts, tables and diagrams that provide the values of the properties for various ranges of temperature and pressure. For example the Mollier diagram gives H vs S curves using T and P as a parameters; steam tables provide the properties like saturation pressure, specific volumes, specific enthalpy and specific entropy for the steam. The estimation of thermodynamic properties using the data available in the form of charts, tables and diagrams requires frequent interpolation. Moreover, the estimation of some properties, which are not presented in the charts and tables, requires knowledge of the derivatives of some other properties, which cannot be evaluated with reasonable accuracy. On the other hand EOS can be directly used for the calculation of various thermodynamic properties. Moreover some EOS are capable of expressing liquid as well as the vapor phase behaviors and use only three compound dependent parameters like critical temperature (T_c), critical pressure (P_c) and acentric factor (ω).

In the present work, attempts have been made to develop a computer software for the prediction of the thermodynamic properties using four pressure explicit cubic EOS. The software is developed using Borland C++ programming language on MS-DOS operating system. It can predict the thermodynamic properties for pure substances as well as for multi-component mixtures. For the pure components it can predict molar volume, departure functions, fugacity, saturation pressure, saturation temperature, vapor enthalpy and vapor entropy. For multi-component mixtures it can predict molar volume, departure functions, fugacity, fugacity of the individual components in the mixture (partial fugacity). In addition to performing phase equilibrium calculations that is bubble point, and dew point calculation the software also predicts the constant pressure Vapor-Liquid Equilibrium (VLE) data for binary systems using various activity coefficient models. The software provides an option to choose anyone of the following four cubic EOS.

- ➤ van der Waals equation of state
- ➤ Redlich-Kwong equation of state
- ➤ Soave- Redlich-Kwong equation of state and

➢ Peng-Robinson equation of state

For the predication of constant pressure VLE data the software provides the following options for the activity coefficient models.

➢ Margules equation
➢ van Laar equation
➢ Wilson equation and
➢ Non-Random Two Liquid (NRTL) equation and
➢ UNIFAC model (A group contribution model)

The software has an inbuilt database for 250 compounds and can process the relevant information to display the desired thermodynamic property at specified temperature and pressure. If one selects a compound that is not included in the database, the user has to furnish the compound related parameters. For the constant pressure VLE data using activity coefficient models the user have to provide the parameter related to the model chosen. However, for the UNIFAC model, a separate database containing more then 70 compounds is included in the software.

Chapter 2

THEORY

For the estimation of thermodynamic properties various theoretical and empirical relations, although not generally valid, are in common use. Most of the better estimation methods use equations based on theory coupled with empirical correlation of the constants that are not provided by the theory. Introduction of empiricism into parts of a theoretical relation provides a powerful method for developing a reliable correlation. The best example is the various equations of state, which are most widely used for the prediction of thermodynamic properties. The main advantages of using an equation of state are already discussed in the previous chapter.

The first section of this chapter deals with the various equations of state followed by the estimation methods for thermodynamic properties.

2.1 Equation Of State:

The most convenient method of representing the *P-v-T* behavior of a substance is through a mathematical expression of the type

$$f(P, v, T) = 0 \tag{2.1}$$

This type of relation is called Equation Of State (EOS). The simplest and the oldest volumetric EOS is the ideal gas equation, given by

$$PV = nRT \tag{2.2}$$

where, R is the universal gas constant.

The Eq. (2.2) is based on the assumptions that volume occupied by the molecules themselves is negligible, molecules are independent of each other and do not exert any attractive force. The ideal gas equation is valid only at sufficiently low

density. Moreover, it does not predict the occurrence of a vapor liquid phase transition. As the ideal gas law is only an approximation or idealization to the behavior of the gases and is applicable only at low densities, several attempts have been made to accurately represent the behavior of real gases and a large number of EOS have been proposed. Following are the most commonly used cubic EOS.

> Van der Waals Equation of state (vdW)
> Redlich-Kwong Equation of state (RK)
> Soave- Redlich-Kwong Equation of state (SRK)
> Peng-Robinson Equation of state (PR)

2.1.1 van der Waals Equation of state

The van der Waals EOS, proposed in 1873, was the first EOS capable of representing the vapor liquid coexistence. It is given by

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \tag{2.3}$$

The EOS parameter a is a measure of attractive forces between the molecules, and the parameter b is the excluded volume i.e. the volume that is not available for the molecular motion due to the presence of the other molecule. The parameters a and b can be determined using the fact that the critical isotherm exhibits a point of inflection. That is, at the critical point

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0 \tag{2.4}$$

Using Eq. (2.3) and Eq. (2.4) one can obtain

$$a = \frac{27R^2 T_c^2}{64P_c} \tag{2.5}$$

and

$$b = \frac{RT_c}{8P_c} \tag{2.6}$$

where, T_C and P_C are the critical temperature and pressure, respectively.

2.1.2 Redlich-Kwong Equation of state

An important modification of the vdW EOS was made by Redlich and Kwong (1949). The RK EOS retains the original repulsive term with the addition of a temperature dependent attractive term. The RK EOS is given as

$$P = \frac{RT}{v-b} - \frac{a}{T^{1.5}} \frac{1}{v(v+b)} \tag{2.7}$$

Where

$$a = 0.42748 \frac{R^2 T_c^{2.5}}{P_c} \tag{2.8}$$

$$b = 0.08664 \frac{RT_c}{P_c} \tag{2.9}$$

2.1.3 Soave- Redlich-Kwong Equation of state

Soave (1972) proposed a modification to the RK EOS replacing the term $\frac{a}{T^{1.5}}$

with a more general term $a\ (T)$, that is

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \tag{2.10}$$

Where

$$a(T) = a_c \alpha(T) \tag{2.11}$$

$$\alpha(T) = \left[1 + \left(0.48 + 1.574\omega - 0.176\omega^2\right)\left(1 - \sqrt{T_r}\right)\right]^2 \tag{2.12}$$

And ω is the Pitzer (1977) acentric factor, which is defined as

$$\omega = -\log P_r^s \big|_{T_r = 0.7} - 1.0 \tag{2.13}$$

where, P_r^S (reduced vapor pressure at $T_r = 0.7$) $= P^S/P_c$

The SRK EOS predicts the vapor pressure of a large number of hydrocarbons, which are fairly close to the experimental data.

2.1.4 Peng-Robinson Equation Of State

Peng and Robinson (1976) used a different volume dependence to give slightly improved liquid volume ($Z_c=0.307$) and redefined the term $a(T)$. The PR EOS is given by

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$$ (2.14)

Where,

$$a = 0.45724\frac{R^2 T_c^2 \alpha}{P_c}$$ (2.15)

$$b = 0.07780\frac{RT_c}{P_c}$$ (2.16)

$$\sqrt{\alpha} = 1 + S\left(1 - \sqrt{T_r}\right)$$ (2.17)

$$S = 0.37464 + 1.5426\omega - 0.269\omega^2$$ (2.18)

2.2 Calculation of thermodynamic properties for pure substances

The four cubic EOS, discussed in the previous section can be expressed in a general form as

$$P = \frac{RT}{(v-b)} - \frac{a}{(v^2 + ubv + wb^2)}$$ (2.19)

Where, u and w are constants associated with a given EOS. The values of u and w for the four EOS are presented in Table 2.1.

The Eq. (2.19) can be rewritten as

$$Z^3 + \alpha Z^2 + \beta Z + \gamma = 0 \qquad (2.20)$$

Where,

$$Z = \frac{Pv}{RT} \qquad (2.21)$$

$$\alpha = -1 - B + uB \qquad (2.22)$$

$$\beta = A + \omega B^2 - uB - uB^2 \qquad (2.23)$$

$$\gamma = -AB - \omega B^2 - \omega B^3 \qquad (2.24)$$

$$A = \frac{aP}{(RT)^2} \qquad (2.25)$$

$$B = \frac{bP}{RT} \qquad (2.26)$$

Table 1.0 *Values of u, w, α, β and γ cubic equations of state*

Equation of state	u	w	α	β	γ
Van der Waals	0	0	-1-B	A	-AB
Redlich-Kwong	1	0	-1	A- B-B^2	-AB
Soave-Redlich-kwong	1	0	-1	A- B-B^2	-AB
Peng-Robinson	2	-1	-1+B	A- 2B-3B^2	-AB + B^2 +B^3

The Eq. (2.20) is the general form of the four cubic EOS. The calculation method presented in the following sub-section uses this general form of EOS.

2.2.1 Calculation of molar volume

The volume of the liquid or vapor can be calculated by adopting an iterative technique. However, such calculations are tedious and hence one can use Cardan's method to determine the roots of cubic EOS.

The Eq. (2.20) can be solved using Cardan's method and depending upon the pressure and temperature one can get

- ✓ Only one real and positive root. If $T > Tc$ it corresponds to vapor compressibility factor Z_v, else it will corresponds to either liquid or vapor compressibility factor.

- ✓ Three real and positive roots, two of them are equal. The smallest value of Z corresponds to Z_l and the largest value corresponds to Z_v.

- ✓ Three real and unequal roots. The smallest value of Z corresponds to Z_l and the largest value corresponds to Z_v. The intermediate value has no physical significance.

These values of Z_v and Z_l are then used to predict vapor and liquid volumes respectively using Eq. (2.21).

2.2.2 Calculation of Enthalpy and Entropy Departure Functions

The enthalpy departure, which is the difference between the enthalpy of a real fluid and the enthalpy of the ideal fluid at the same temperature and pressure, is given by

$$\left(h - h^0\right)_{T,P} = RT(Z-1) + \int_{v=\infty}^{v}\left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]_T dv \qquad (2.27)$$

Similarly, the entropy departure is the difference between the entropy of the real fluid and the entropy of the ideal fluid at the same temperature and pressure and for the pressure explicit cubic EOS it is given by

$$\left(s - s^0\right)_{T,P} = R\ln Z + \int_{v=\infty}^{v}\left[\left(\frac{\partial P}{\partial T}\right)_v - \frac{R}{v}\right]_T dv \qquad (2.28)$$

Following are the expressions for the enthalpy departure and entropy departure functions using the four cubic EOS.

vdW EOS

$$(h - h^0)_{T,P} = Pv - RT - \frac{a}{v} \qquad (2.29)$$

$$(s - s^0)_{T,P} = R \ln \frac{P(v-b)}{RT} \qquad (2.30)$$

RK EOS

$$(h - h^0)_{T,P} = RT(Z-1) - \frac{3a}{2b} \ln\left(\frac{Z+B}{Z}\right) \qquad (2.31)$$

$$(s - s^0)_{T,P} = R \ln(Z-B) - \frac{a}{2bT} \ln\left(\frac{Z+B}{Z}\right) \qquad (2.32)$$

SRK EOS

$$(h - h^0)_{T,P} = RT(Z-1) + \frac{T\left(\frac{\partial a}{\partial T}\right) - a}{b} \ln\left(\frac{Z+B}{Z}\right) \qquad (2.33)$$

$$(s - s^0)_{T,P} = R \ln(Z-B) + \frac{1}{b}\left(\frac{\partial a}{\partial T}\right) \ln\left(\frac{Z+B}{Z}\right) \qquad (2.34)$$

where
$$\left(\frac{\partial a}{\partial T}\right) = -\frac{0.42748 R^2 T_c^2}{P_c}\sqrt{\frac{\alpha}{TT_c}} \qquad (2.35)$$

PR EOS

$$(h - h^0)_{T,P} = RT(Z-1) + \frac{T\left(\frac{\partial a}{\partial T}\right) - a}{2\sqrt{2}b} \ln\left(\frac{Z+B(1+\sqrt{2})}{Z+B(1-\sqrt{2})}\right) \qquad (2.36)$$

$$(s - s^0)_{T,P} = R \ln(Z-B) + \frac{1}{2\sqrt{2}b}\left(\frac{\partial a}{\partial T}\right) \ln\left(\frac{Z+B(1+\sqrt{2})}{Z+B(1-\sqrt{2})}\right) \qquad (2.37)$$

where,
$$\left(\frac{\partial a}{\partial T}\right) = -\frac{0.45724 R^2 T_c^2}{P_c}\sqrt{\frac{\alpha}{TT_c}} \qquad (2.38)$$

The enthalpy and entropy departures can be calculated using the above equations.

2.2.3 Calculation of Fugacity and Fugacity Coefficient

For an ideal gas, the change in Gibbs free energy is given by

$$dg^0 = \frac{RT}{P}dP = RTd\ln P \tag{2.39}$$

Eq. (2.39) is not valid for a real gas. However, its form is quite useful and thus a new parameter fugacity is defined such that the form of the Eq.(2.39) is retained for real fluids. Therefore, the fugacity is defined as

$$dg = RTd\ln f \tag{2.40}$$

and
$$\frac{f}{P} \rightarrow 1 \text{ as } P \rightarrow 0 \tag{2.41}$$

The ratio of the fugacity to the pressure is defined as the fugacity coefficient ϕ that is

$$\phi = \frac{f}{p} \tag{2.42}$$

To estimate the fugacity, from the above discussed four cubic EOS, the following relation between the fugacity coefficient, Gibbs free energy and the departure function can be used.

$$\ln\phi = \frac{g - g^0}{RT} = \frac{h - h^0}{RT} - \frac{T(s - s^0)}{RT} \tag{2.43}$$

By substituting the enthalpy and entropy departure presented in the previous section, Eq. (2.29) to Eq. (2.38), in the Eq. (2.43) the following relations for the fugacity coefficient can be obtained.

vdW EOS

$$\ln \phi = Z - 1 - \ln \frac{P(v-b)}{RT} - \frac{a}{RTv} \qquad (2.44)$$

RK EOS

$$\ln \phi = Z - 1 - \ln(Z - B) - \frac{a}{bRT} \ln\left(\frac{Z+B}{Z}\right) \qquad (2.45)$$

SRK EOS

$$\ln \phi = Z - 1 - \ln(Z - B) - \frac{a}{bRT} \ln\left(\frac{Z+B}{Z}\right) \qquad (2.46)$$

PR EOS

$$\ln \phi = Z - 1 - \ln(Z - B) - \frac{a}{2\sqrt{2}bRT} \ln\left(\frac{Z+B(1+\sqrt{2})}{Z+B(1-\sqrt{2})}\right) \qquad (2.47)$$

2.2.4 Calculation of Saturation Temperature and Saturation Pressure

The criterion for equilibrium can be used for the calculation of saturation pressure and saturation temperature of a liquid. If a liquid is in equilibrium with its own vapor, the criterion of equilibrium gives

$$f^l = f^v \qquad (2.48)$$

Where,

f^l and f^v are the fugacity of the liquid and vapor phases respectively.

An iterative technique can be used to calculate the saturation pressure (or saturation temperature). For the calculation of saturation pressure an initial guess value of P is assumed at the specified temperature T ($< T_C$). Then at these P and T values, depending upon the choice of EOS, f^l and f^v can be calculated using the Eq. (2.44) to Eq. (2.47) discussed in the previous section. Subsequently, it is checked whether the criterion of equilibrium specified by Eq. (2.48) is satisfied or not, if the criterion is satisfied then the guess value P is the required saturation pressure. If it is not satisfied, the guess value will be modified using following equation.

$$P(new) = P\frac{f^l}{f^v} \qquad (2.49)$$

Similar procedure can be employed to calculate saturation temperature.

2.2.5 Calculation of Enthalpy and Entropy of Vapor

For the calculation of enthalpy and entropy the four step path shown in the figure below can be used.
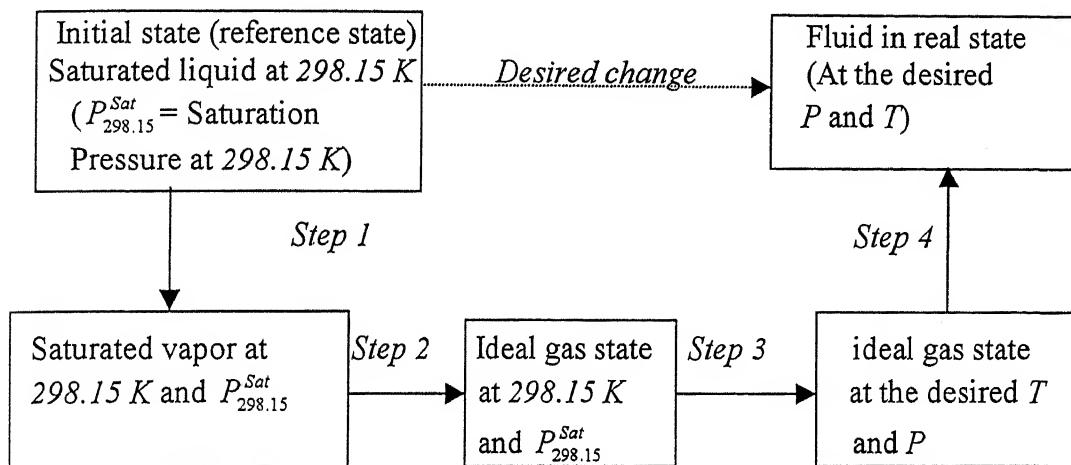
Fig. 2.1 *Four-step path for the estimation of h and s.*

The reference state is assumed to be saturated liquid at *298.15 Kelvin (25 ^0C)*. At this reference state the internal energy and entropy of the substance are assumed to be zero. Then

$$h^o = u^o + P^{sat}v \qquad (2.50)$$

Where,

u^o = Internal energy at reference state.

P^{sat} = Saturation pressure at *298.15* K

v = Molar volume at *298.15* K and P^{sat}

which gives

$$h^o = P^{sat}v \qquad (2.51)$$

In the *step 1* the substance is vaporized at *298.15 K* and at saturation pressure so change in enthalpy is equal to the enthalpy of vaporization at *298.15 K*. To calculate the enthalpy of vaporization (Δh_v) at *298.15 K* initially, the enthalpy of vaporization is calculated, at normal boiling point of the substance, using Riedel correlation given by

$$\Delta h_{vn} = 1.093RT\left[T_{br}\frac{\ln P_c - 1.013}{0.930 - T_{br}}\right] \qquad (2.52)$$

Then the Watson's correlation given below is used to determine Δh_v.

$$\Delta h_v = \Delta h_{v2} = \Delta h_{v1}\left(\frac{1 - T_{r2}}{1 - T_{r1}}\right)^{0.38} \qquad (2.53)$$

The change in entropy can then be calculated by the following relation

$$\Delta s_1 = -\frac{\Delta h_v}{T} \qquad (2.54)$$

In the *step 2* the substance is brought to the ideal gas state from the real gas state at the same temperature and pressure. The changes in enthalpy and entropy can be estimated from the knowledge of departure functions.

In the *step 3* the substance is brought to the desired T and P in ideal gas state and the changes can be estimated using the constant pressure heat capacity data. The following equations can be used for the calculation of the entropy and enthalpy changes in the *step 3*.

$$\Delta h_3 = \int_{T1}^{T2} C_P^0 dT \qquad (2.55)$$

$$\Delta s_3 = \int_{T1}^{T2} C_P^0 dT - R\ln\frac{P_2}{P_1} \qquad (2.56)$$

In the *step 4* the substance in the ideal gas state at T and P is changed to the real gas sate at the same temperature and pressure. And the changes in the enthalpy and entropy can be calculated from the knowledge of departure functions.

Finally the enthalpy and entropy are obtained by summing all the enthalpy and entropy changes in the *step 1* to *step 4*.

$$h = h_0 + h_1 + h_2 + h_3 + h_4 \qquad (2.57)$$

$$s = s_1 + s_2 + s_3 + s_4 \qquad (2.58)$$

2.3 Calculation of Thermodynamic Properties of Mixture

The thermodynamic properties of the mixture can be obtained by modifying the method used for a real gas ~~mixture~~. The modification needs additional composition variable as an input parameter. The constants that characterize the pure fluid are replaced by the mixture constants. The relation which expresses the mixture constants in terms of pure fluid constants are called mixing rules. Usually the mixing rules are empirical and their validity rests upon the agreement between predicted and experimentally measured properties. The most commonly used mixing rule for the cubic EOS (vdW, RK, SRK and PR) is the van der Waals mixing rule.

In the van der Waals mixing rule the mixture parameters a_m and b_m are expressed as

$$a_m = \sum_{i,j} y_i y_j \sqrt{a_i a_j} \left(1 - K_{ij}\right) \tag{2.59}$$

$$b_m = \sum_i y_i b_i \tag{2.60}$$

where $K_{i,j}$ is the binary interaction parameter between the components i and j.

The binary interaction parameter $K_{i,j}$ is introduced to obtain better agreement between the predicted and experimental results. Usually this parameter is obtained by fitting the equation of state to the experimental data. The interaction parameter $K_{i,j}$ assumes values close to zero and in the absence of any data it can be set to zero.

The mixture molar volume, departure functions and fugacity can be calculated using the methods disused in *section 2.2*. The prediction of the partial fugacity is discussed in the following sub-section.

2.3.1 Calculation of Partial Fugacity

The partial fugacity $\hat{f}_i$ that is the fugacity of component i in the mixture is defined as

$$dg_i = \bar{v}_i dP = RT d\ln \hat{f}_i \qquad \text{at constant } T \qquad (2.61)$$

or
$$\left(\bar{g}_i - \bar{g}_i{}^o\right) = RT \ln\left(\frac{\hat{f}_i}{f_i{}^o}\right) = RT \ln\left(\frac{\hat{f}_i}{y_i P}\right) = \int_{P=0}^{P} \left(\bar{v}_i - \frac{RT}{P}\right) dP \qquad (2.62)$$

And
$$\frac{\hat{f}_i}{y_i P} \rightarrow 1 \qquad \text{as} \qquad P \rightarrow 0 \qquad (2.63)$$

where, $f_i{}^o$ is the fugacity of the pure component i in the reference state, where it behaves like an ideal gas.

The partial fugacity of component i in a mixture for the four cubic EOS can be estimated by the relations given below.

vdW EOS

$$\ln \hat{\phi}_i = \frac{b_i}{v-b} - \ln\left[Z\left(1 - \frac{b}{v}\right)\right] - \frac{2\sqrt{a a_i}}{RTv} \qquad (2.64)$$

RK EOS

$$\ln \hat{\phi}_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) + \frac{a}{bRT}\left[\frac{b_i}{b} - 2\sqrt{\frac{a_i}{a}}\right]\ln\left[\frac{Z+B}{Z}\right] \qquad (2.65)$$

SRK EOS

$$\ln \hat{\phi}_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) + \frac{a}{bRT}\left[\frac{b_i}{b} - 2\sqrt{\frac{a_i}{a}}\right]\ln\left[\frac{Z+B}{Z}\right] \qquad (2.66)$$

PR EOS

$$\ln \hat{\phi}_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) + \frac{a}{2\sqrt{2}RT}\left[\frac{b_i}{b} - 2\sqrt{\frac{a_i}{a}}\right]\ln\left[\frac{Z+B\left(1+\sqrt{2}\right)}{Z+B\left(1-\sqrt{2}\right)}\right] \qquad (2.67)$$

where
$$\frac{b_i}{b} = \frac{\left(\dfrac{T_{Ci}}{P_{Ci}}\right)}{\sum_i \left(\dfrac{y_i T_i}{P_{Ci}}\right)} \qquad (2.68)$$

To estimate the partial fugacity of a component in a mixture, first the pure component constants a_i and b_i are calculated. Then using the vdW-mixing rule the mixture

parameters are calculated. The volume, compressibility factor and $\hat{\phi}_i$ are calculated using Eq. (2.64) to Eq. (2.68) depending upon the choice of EOS.

2.4 Phase Equilibrium Calculation

For a closed system consisting of co-existing vapor and liquid phases, each phase containing C components, the criterion for equilibrium between the two phases is given by

$$f_i^l = f_i^v \qquad \left[i = 1,2,3,........,C\right] \qquad (2.69)$$

Using the concept of fugacity, fugacity coefficient, activity and activity coefficient, Eq. (2.69) can be transformed to give

$$\gamma_i x_i P_i^{sat} = \frac{\phi_i^v}{\phi_i^{sat}} y_i P \exp\left\{\frac{v_i^l \left(P - P_i^{sat}\right)}{RT}\right\} \qquad \left[i = 1,2,3,........,C\right] \qquad (2.70)$$

where,

ϕ_i^v = Fugacity coefficient of component i in the vapor phase solution and

ϕ_i^{sat} = Fugacity coefficient of component i at saturation pressure.

Eq. (2.69) is called the basic equation of vapor liquid equilibrium and provides a systematic means of analyzing vapor-liquid equilibrium data. The analysis of vapor-liquid equilibrium data can be divided into the following four problems.

Problem Type	Known	To estimate
➢ Bubble pressure calculation	T, x_i's	P, y_i's
➢ Bubble temperature calculation	P, x_i's	T, y_i's
➢ Dew pressure calculation	T, y_i's	P, x_i's
➢ Dew temperature calculation	P, y_i's	T, x_i's

2.4.1 Bubble point and Dew point Calculation using EOS

For bubble point and dew point calculation basic equation of vapor liquid equilibrium, Eq. (2.70), can be rewritten as

$$\hat{\phi}_i^{\,l} x_i = \hat{\phi}_i^{\,v} y_i \quad [i = 1,2,3,\ldots\ldots,C] \tag{2.71}$$

Or
$$K_i = \frac{y_i}{x_i} = \frac{\hat{\phi}_i^{\,l}}{\hat{\phi}_i^{\,v}} \tag{2.72}$$

In addition to this, the values of x_i and y_i must satisfy the stoichiometric conditions given by

$$\sum_{i=1}^{C} x_i = 1 \tag{2.73}$$

and
$$\sum_{i=1}^{C} y_i = 1 \tag{2.74}$$

$\hat{\phi}_i^{\,l}$ and $\hat{\phi}_i^{\,v}$ can be calculated using equations discussed in *section 2.3.1*. An iterative scheme can be used using the Eq. (2.72) for the bubble point and dew point calculation.

2.4.2 Prediction of VLE data - Excess Gibbs Free Energy Model

The VLE data can be predicted by using Eq. (2.70). At low to moderate pressure the Poynting correction factor can be assumed as unity and ($\hat{\phi}_i^{\,v} / \phi_i^{\,sat}$) is approximately equal to unity. Hence, Eq. (2.70) takes the following form

$$\gamma_i x_i P_i^{\,sat} = y_i P \tag{2.75}$$

The Eq. (2.75) can be used for the prediction of constant pressure VLE data using various excess Gibbs free energy models discussed in the following sub section.

2.4.2.1 Excess Gibbs Free Energy Models

The behavior of almost all liquid solutions cannot be adequately expressed in terms of an equation of state. For such mixtures, attempts have been made to estimate the excess Gibbs free energy either empirically or semi empirically leading to several models for excess Gibbs free energy. In this section the excess Gibbs free energy models for binary solutions are presented.

2.4.2.1.1 Margules Equation

The simplest expression for the excess Gibbs free energy for a binary solution is the two suffix Margules equation which is given by

$$\left(g^E / RT\right) = Ax_1 x_2 \tag{2.76}$$

Where A is an adjustable parameter which assume a constant value over a range of temperature and differ from system to system. Eq. (2.76) can be used to obtain the following equations relating the activity coefficients explicitly to liquid phase mole fractions.

$$\ln \gamma_1 = Ax_2^{\,2} \tag{2.77}$$

and $\quad \ln \gamma_2 = Ax_1^{\,2} \tag{2.78}$

2.4.2.1.2 van Laar Equation

The excess Gibbs free energy of a binary liquid solution can be represented by the two parameters van Laar Equation which is given by

$$\left(g^E / RT\right) = \frac{A x_1 x_2}{x_1 \left(A/B\right) + x_2} \tag{2.79}$$

The Eq. (2.79) can be manipulated to yield the following activity coefficient correlation.

$$\ln \gamma_1 = \frac{A}{\left[1 + \left(A/B\right)\left(x_1 / x_2\right)\right]^2} \tag{2.80}$$

and
$$\ln \gamma_2 = \frac{B}{\left[1 + \left(B/A\right)\left(x_2 / x_1\right)\right]^2} \tag{2.81}$$

2.4.2.1.3 Wilson Equation

For mixtures in which the components differ from each other in molecular size and the interaction between the like and unlike molecules are different, Wilson proposed the following expression for the excess Gibbs free energy of a binary solution.

$$\left(g^E / RT\right) = x_1 \ln\left(x_1 + V_{12} x_2\right) - x_2 \ln\left(x_2 + V_{21} x_1\right) \tag{2.82}$$

The Eq.(2.82) leads to the following activity coefficient correlations.

$$\ln \gamma_1 = -\ln\left(x_1 + V_{12} x_2\right) + x_2 \left\{ \frac{V_{12}}{x_1 + V_{12} x_2} - \frac{V_{21}}{x_1 + V_{21} x_2} \right\} \tag{2.83}$$

and
$$\ln \gamma_2 = -\ln\left(x_2 + V_{21} x_1\right) + x_2 \left\{ \frac{V_{12}}{x_1 + V_{12} x_2} - \frac{V_{21}}{x_1 + V_{21} x_2} \right\} \tag{2.84}$$

2.4.2.1.4 Non-Random Two Liquid (NRTL) Equation

The NRTL equation proposed by Renon is applicable to partially miscible as well as completely miscible systems. The excess Gibbs free energy of a binary mixture is given by

$$\left(g^E / RT\right) = x_1 x_2 \left\{ \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right\} \tag{2.85}$$

Where

$$\tau_{12} = (g_{12} - g_{22})/RT \tag{2.86}$$

$$\tau_{21} = (g_{21} - g_{11})/RT \tag{2.87}$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \tag{2.88}$$

$$G_{21} = \exp(-\alpha_{12}\tau_{21}) \tag{2.89}$$

The parameter α_{12} is introduced to take into account the non-randomness of the mixture. If $\alpha_{12}=0$, the mixture is completely random and equation Eq. (2.85) reduces to two suffix Margules equation. Usually α_{12} varies from *0.20* to *0.47* and in the absence of any information $\alpha 12$ can be taken as *0.30*. The parameter g_{ij} is introduced to take into account the energy of interaction between molecules of components *i* and *j* and it is analogous to Wilson's parameter λ_{ij}. The activity coefficients can be derived from Eq. (2.85) and are given by

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left\{ \frac{G_{21}}{x_1 + x_2 G_{21}} \right\}^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \tag{2.90}$$

and

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left\{ \frac{G_{12}}{x_2 + x_1 G_{12}} \right\}^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \tag{2.91}$$

2.4.3 Prediction of VLE data using UNIFAC method

Fredenslund, Jones, and Prusnitz first presented the UNIFAC GROUP contribution method. It was further developed by Fredenslund et. al., Gmehlig and Rasmussen, for use in practice. It is based on the concept that a liquid mixture may be considered as a solution of the structural units from which the molecules are formed rather then the solution of the molecules themselves (Concept given by Wilson and Deal in 1960). These structural units are called subgroups. To calculate the partial molar excess Gibbs free energies g_i^E and thus to calculate the activity coefficients, the size parameter (volume and area parameters) and binary interaction parameter for each pair of subgroups are required. Size parameter will take care of shape and size of molecules and the interaction parameter gives the binary interaction between the two subgroups.

The UNIFAC method for predicting liquid phase activity coefficients is essentially based on the UNIQUAC equation. In the UNIFAC method the activity coefficient consists of two parts - $\ln \gamma_i^C$ (combinatorial) and $\ln \gamma_i^R$ (residual).

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{2.92}$$

The combinatorial part of the activity coefficient is given by

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \tag{2.93}$$

and the residual part is given by

$$\ln \gamma_i^R = \sum v_k^{(i)} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right) \tag{2.94}$$

Where

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{mk}}{\sum_n \theta_m \psi_{nm}} \right] \tag{2.95}$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} = \text{Surface area fraction of group } m \tag{2.96}$$

$$\psi_{mn} = \exp \left(-\frac{u_{mn} - un}{RT} \right) = \exp \left(-\frac{a_{mn}}{T} \right) \tag{2.97}$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \tag{2.98}$$

$$r_i = \sum_k v_k^{(i)} R_k \tag{2.99}$$

$$q_i = \sum_k v_k^{(i)} Q_k \tag{2.100}$$

Q_k = group volume parameter

R_k = group area parameter

x_m = mole fraction of group m in the mixture

a_{mn} = interaction parameter (in Kelvin). $a_{mn} \neq a_{nm}$

u_{mn} = measure of interaction energy between groups m and n

Γ_k = group residual coefficient and

$\Gamma_k^{(i)}$ = residual activity coefficient of group k in a reference solution containing only molecules of type i.

The parameters required for the calculation of activity coefficient using UNIFAC method are group area and volume parameters (R_k, Q_k) and the interaction parameter (a_{mn}) for each pair of subgroups.

Chapter 3

COMPUTER PROGRAM

The software to calculate thermodynamic properties contains, in all *17* programs, which are coupled by a program named MASTER program. Each program is responsible for a unique property prediction. Due to the excessive code length (Approximately *9000* lines), it is not possible to provide source code for the software- instead simplified flowcharts are provided in this chapter. The programs for property estimation uses the methods described in *Chapter 2*.

The problems of predicting the thermodynamic properties are divided in to several small parts to provide necessary flexibility and to avoid the repeated coding for the same calculation. For example calculation of molar volume requires

1. The identification of EOS i.e. values of u and w,
2. Evaluation of EOS constants a, b, A, B, S and α
3. Finally these u, w, a, b, A, B, S and α are used in the appropriate equation for the calculation of Molar Volume.

The first two tasks are related with individual EOS, which are to be used for the calculation, and are common for almost all the programs. Hence, two different subroutines are developed (Get_UW_EOS for u and w values and Get_AB_EOS for calculating EOS parameters a, b, S and α). Similarly, all other properties calculations are divided into several small parts with the objective of reducing the code length and to provide flexibility.

In this chapter flowcharts are provided for the individual property estimation methods followed by the flowcharts of all the subroutines, which are used in property estimation.

3.1 Calculation of Thermodynamic Properties (Flowcharts) :-

Flowchart for the calculation of volume

```
                    ┌──────────────┐
                    │    START     │
                    └──────────────┘
                           │
                           ▼
                    ╱─────────────╱
                   ╱ Read T, P, EOS╱
                  ╱   Tc, Pc, ω   ╱
                 ╱───────────────╱
                           │
                           ▼
              ┌──┬──────────────────┬──┐
              │  │  Call Get_UW_EOS │  │
              │  │(Provide parameter u and w)│
              └──┴──────────────────┴──┘
                           │
                           ▼
              ┌──┬──────────────────┬──┐
              │  │  Call Get_AB_EOS │  │
              │  │(Calculate a, b, S and α)│
              └──┴──────────────────┴──┘
                           │
                           ▼
              ┌──┬──────────────────┬──┐
              │  │   Call Volume    │  │
              │  │(Calculate volume)│  │
              └──┴──────────────────┴──┘
                           │
                           ▼
                    ╱──────────────╱
                   ╱ Print vˡ and vᵛ╱
                  ╱───────────────╱
                           │
                           ▼
                    ┌──────────────┐
                    │    STOP      │
                    └──────────────┘
```

Read T, P, EOS T_c, P_c, ω

Call Get_UW_EOS (Provide parameter u and w)

Call Get_AB_EOS (Calculate a, b, S and α)

Call Volume (Calculate volume)

Print v^l and v^v
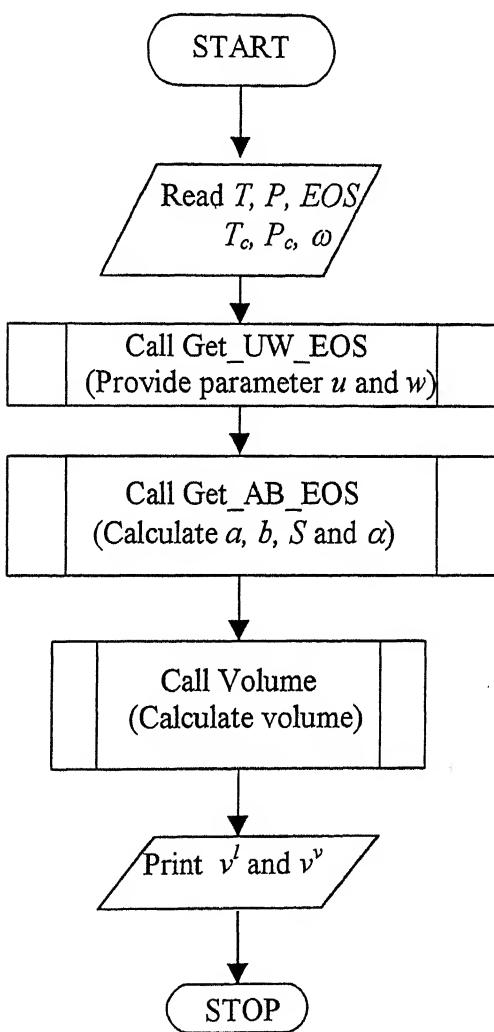
Fig. 3.1 *Flowchart for volume calculation*

Flowchart for the calculation of Enthalpy and Entropy Departure
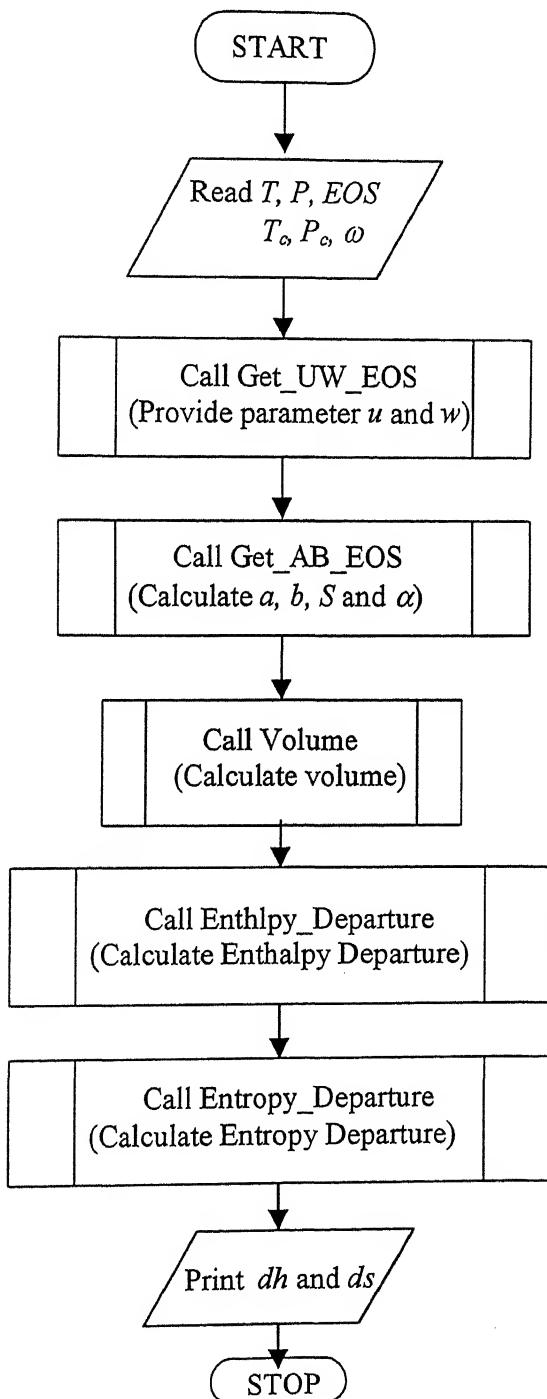
Fig. 3.2 *Flowchart for departure function calculation*

Flowchart for the calculation of Fugacity

START

Read T, P, EOS
T_c, P_c, ω

Call Get_UW_EOS
(Provide parameter u and w)

Call Get_AB_EOS
(Calculate a, b, S and α)

Call Volume
(Calculate volume)

Call Fugacity
(Calculate Fugacity)

Print f^l, f^v
$\phi^l and \phi^v$

STOP
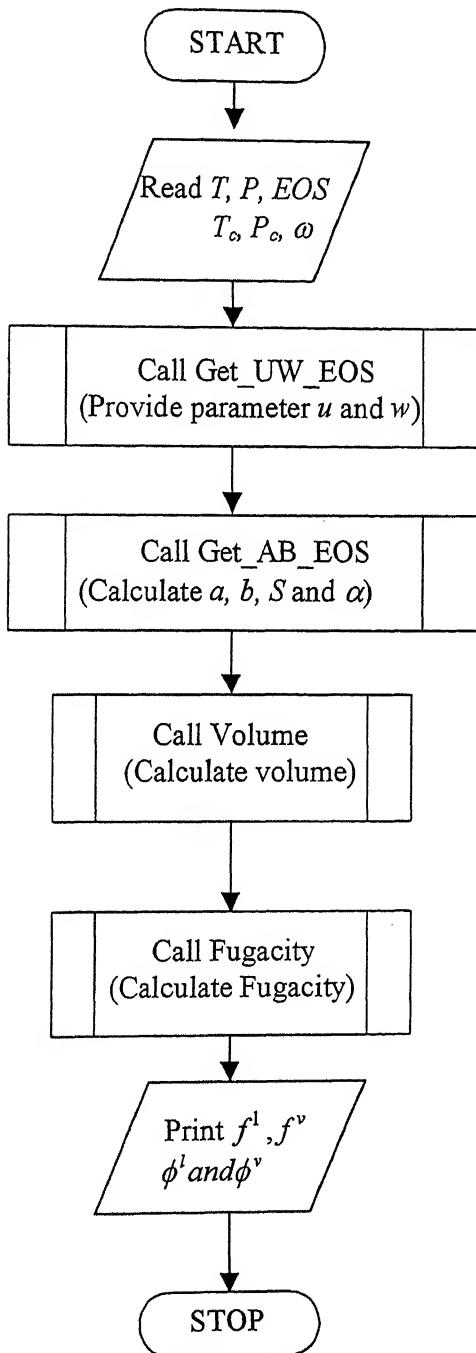
Fig. 3.3 *Flowchart for fugacity calculation*

Flowchart for the calculation of Saturation Pressure

```
           ( START )
               │
               ▼
         ╱ Read T, EOS ╱
        ╱  Tₒ, Pₒ, ω  ╱
               │
               ▼
    ┌──────────────────────────┐
    │    Call Get_UW_EOS        │
    │ (Provide parameter u and w)│
    └──────────────────────────┘
               │
               ▼
    ┌──────────────────────────┐
    │    Call Get_AB_EOS        │
    │ (Calculate a, b, S and α) │
    └──────────────────────────┘
               │
               ▼
        ┌─────────────┐
        │  Guess Pˢᵃᵗ  │
        └─────────────┘
               │
               ▼ ◄─────────────────────────┐
    ┌──────────────────────────┐           │
    │      Call Volume          │           │
    │   (Calculate volume)      │           │
    └──────────────────────────┘           │
               │                           │
               ▼                           │
    ┌──────────────────────────┐           │
    │      Call Fugacity        │           │
    │  (Calculate φˡ and φᵛ)    │           │
    └──────────────────────────┘           │
               │                           │
               ▼                           │
         ◇ Is φˡ = φᵛ ◇ ──No──►  ┌────────────────┐
               │                 │ Pˢᵃᵗ = (φˡ/φᵛ)Pˢᵃᵗ │
              Yes                └────────────────┘
               │
               ▼
        ╱ Print Pˢᵃᵗ ╱
               │
               ▼
           ( STOP )
```

$$P^{sat} = \frac{\phi^l}{\phi^v} P^{sat}$$
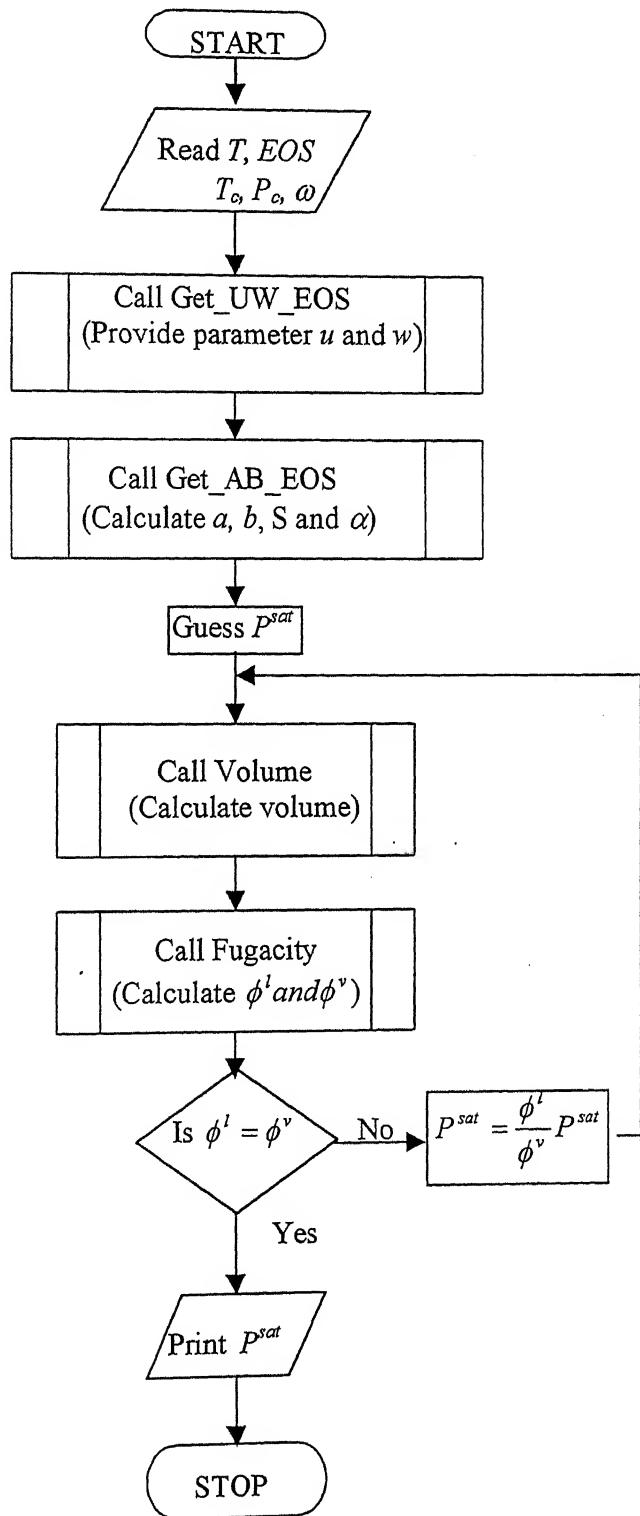
Fig. 3.4 *Flowchart for Saturation pressure calculation*

Flowchart for the calculation of Saturation Temperature

START

Read T, EOS
T_c, P_c, ω

Call Get_UW_EOS
(Provide parameter u and w)

Guess T^{sat}

Set $h=10$

Call Get_AB_EOS
(Calculate a, b, S and α)

Call Volume
(Calculate volume)

Call Fugacity
(Calculate ϕ^l and ϕ^v)

$T = T-h$ <1 Cheek $\dfrac{\phi^l}{\phi^v}$ ≥ 1 $h = h/10$

$T^{sat} = T^{sat}+h$

$= 1$

Print T^{sat}

STOP
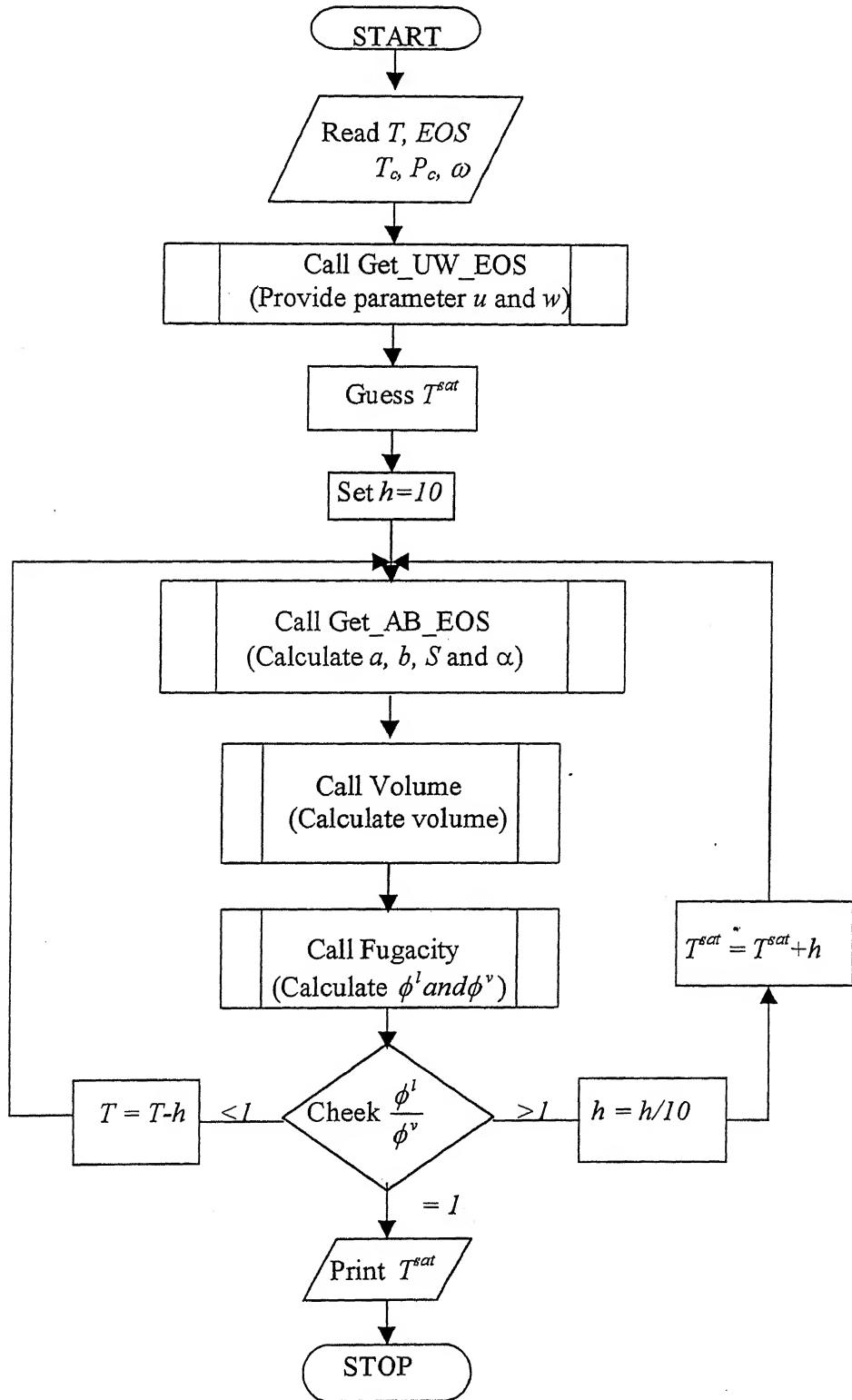
Fig. 3.5 *Flowchart for Saturation temperature calculation*

30

Flowchart for the calculation of Enthalpy and Entropy

```
                    ( START )
                        |
                        v
            / Read T, P, EOS        /
           /  T_c, P_c, ω and NBP  /
                        |
                        v
        |  Call Get_UW_EOS                |
        |  (Provide parameter u and w)    |
                        |
                        v
        |  Call Get_AB_EOS                |
        |  (Calculate a, b, S and α)      |
                        |
                        v
    |  Call Sat_P                              |
    |  (Calculate saturation Pressure at 298.15 K) |
                        |
                        v
```

Call Sat_P
(Calculate saturation Pressure at $298.15\ K$)

Call Volume
(Calculate volume at $298.15\ K$ and $P^{Sat}_{298.15}.\ v$)

Calculate $\quad h^o = P^{Sat}_{298.15} \times v$

Call Watson
(Calculate Enthalpy of vaporization at $298.15\ K$. Δh_1 and Δs_1)

Call Enthlpy_Departure
(Calculate Enthalpy Departure at $298.15\ K$ and $P^{Sat}_{298.15}.\ \Delta h_2$)

(A)

$$\text{A}$$

Call Entropy_Departure
(Calculate Entropy Departure at $298.15\ K$ and $P_{298.15}^{Sat}$. Δs_2)

Call NTPNTH_IDL
(Calculate Enthalpy and Entropy change due to change in state from $298.15\ K$ and $P_{298.15}^{Sat}$ to T and P under ideal gas condition.)

Call Volume
(Calculate volume at T and P)

Call Enthlpy_Departure
(Calculate Enthalpy Departure at T and P .Δh_4)

Call Entropy_Departure
(Calculate Entropy Departure at T and P Δs_4)

Calculate
$h = h^o + \Delta h_1 + \Delta h_2 + \Delta h_3 + \Delta h_4$
$s\ = \Delta s_1 + \Delta s_2 + \Delta s_3 + \Delta s_4$

Print h and s

STOP

Fig. 3.6 *Flowchart for Enthalpy and Entropy calculation*

Flowchart for the calculation of Molar volume of Mixture

```
                    ┌─────────────┐
                    │    START    │
                    └─────────────┘
                           │
                           ▼
             ╱───────────────────────────╱
            ╱ Read      T, P, EOS,       ╱
           ╱ NoComp, T_ci, P_ci and ω_I ╱
          ╱  for i = 1 to NoComp        ╱
         ╱───────────────────────────╱
                           │
                           ▼
           ┌──┬─────────────────────────┬──┐
           │  │     Get UW_EOS          │  │
           │  │(Provide parameter u and w)│  │
           └──┴─────────────────────────┴──┘
                           │
                           ▼
           ┌──┬─────────────────────────┬──┐
           │  │     Get AB_EOS          │  │
           │  │(Calculate a, b, S and α)│  │
           └──┴─────────────────────────┴──┘
                           │
                           ▼
            ┌──┬─────────────────────┬──┐
            │  │   Call vdWMixing    │  │
            │  │ (Calculate a_m, b_m)│  │
            └──┴─────────────────────┴──┘
                           │
                           ▼
          ┌──┬───────────────────────────┬──┐
          │  │      Call Volume          │  │
          │  │(Calculate volume at T and P)│  │
          └──┴───────────────────────────┴──┘
                           │
                           ▼
                  ╱───────────────╱
                 ╱ Print v^l and v^v ╱
                ╱───────────────╱
                           │
                           ▼
                    ┌─────────────┐
                    │    STOP     │
                    └─────────────┘
```
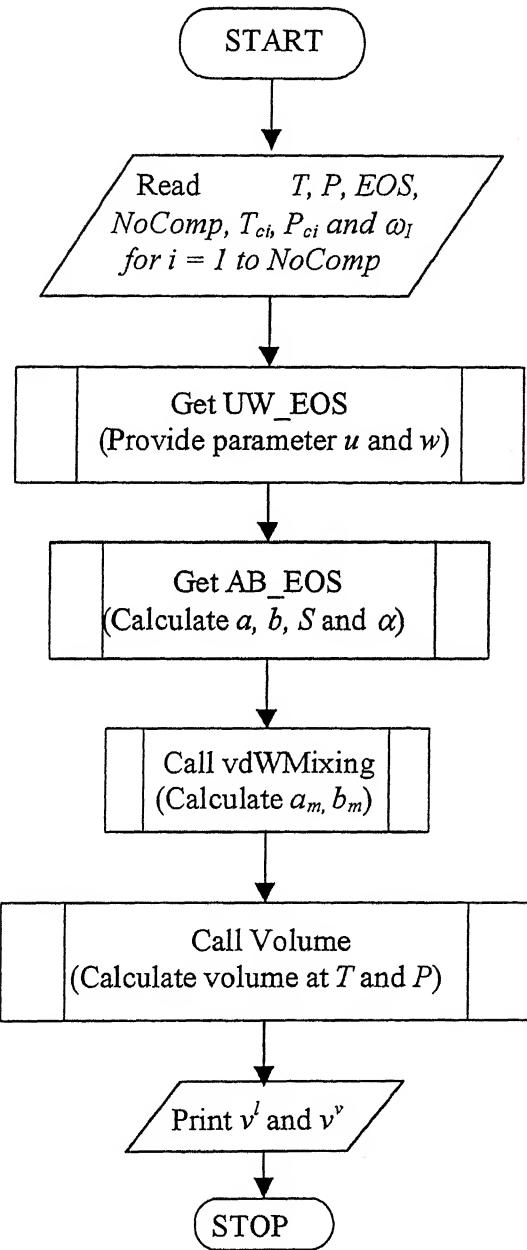
Fig. 3.7 *Flowchart for volume calculation of multi-component mixture*

Flowchart for the calculation of Enthalpy and Entropy departure of Mixture

```
                    ┌─────────────┐
                   ( START )
                    └─────────────┘
                          │
                          ▼
        ╱────────────────────────────────╱
       ╱ Read      T, P, EOS,            ╱
      ╱  NoComp, T_ci, P_ci and ω_I    ╱
     ╱   for i = 1 to NoComp          ╱
    ╱────────────────────────────────╱
                          │
                          ▼
    ┌──┬──────────────────────────┬──┐
    │  │      Get UW_EOS          │  │
    │  │ (Provide parameter u and w)│ │
    └──┴──────────────────────────┴──┘
                          │
                          ▼
    ┌──┬──────────────────────────┬──┐
    │  │      Get AB_EOS          │  │
    │  │ (Calculate a, b, S and α)│  │
    └──┴──────────────────────────┴──┘
                          │
                          ▼
    ┌──┬──────────────────────────┬──┐
    │  │   Call vdWMixing         │  │
    │  │ (Calculate a_m, b_m)     │  │
    └──┴──────────────────────────┴──┘
                          │
                          ▼
    ┌──┬──────────────────────────┬──┐
    │  │   Call Volume            │  │
    │  │ (Calculate volume)       │  │
    └──┴──────────────────────────┴──┘
                          │
                          ▼
        ┌──┬──────────────────┬──┐
        │  │  Call Departure  │  │
        └──┴──────────────────┴──┘
                          │
                          ▼
           ╱──────────────────╱
          ╱ Print dh and ds  ╱
         ╱──────────────────╱
                          │
                          ▼
                  ┌─────────────┐
                 ( STOP )
                  └─────────────┘
```
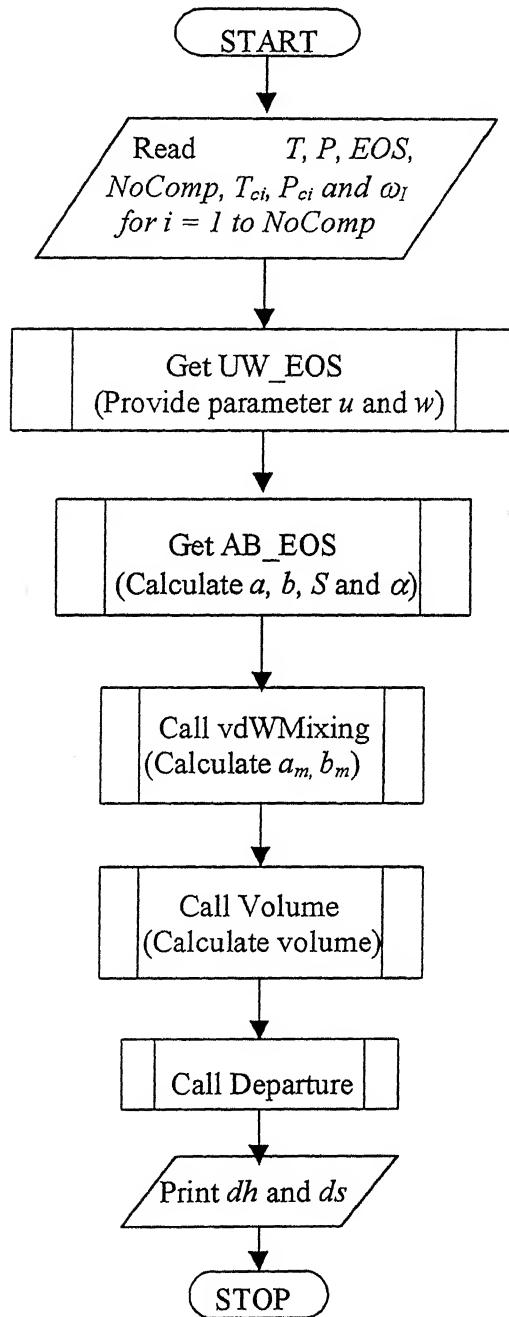
Fig. 3.8 *Flowchart for Departure function calculation of multi-component mixture*

Flowchart for the calculation of fugacity of Mixture

```
                    ╭──────────────╮
                    │    START     │
                    ╰──────────────╯
                           │
                           ▼
          ╱───────────────────────────────╱
         ╱  Read        T, P, EOS,       ╱
        ╱   NoComp, T_ci, P_ci and ω_I  ╱
       ╱    for i = 1 to NoComp        ╱
      ╱───────────────────────────────╱
                           │
                           ▼
         ┌──┬─────────────────────────┬──┐
         │  │      Get UW_EOS         │  │
         │  │ (Provide parameter u and w) │  │
         └──┴─────────────────────────┴──┘
                           │
                           ▼
         ┌──┬─────────────────────────┬──┐
         │  │      Get AB_EOS         │  │
         │  │ (Calculate a, b, S and α) │  │
         └──┴─────────────────────────┴──┘
                           │
                           ▼
         ┌──┬─────────────────────┬──┐
         │  │   Call vdWMixing    │  │
         │  │ (Calculate a_m, b_m)│  │
         └──┴─────────────────────┴──┘
                           │
                           ▼
         ┌──┬─────────────────────────┬──┐
         │  │     Call Volume         │  │
         │  │ (Calculate volume at T and P) │  │
         └──┴─────────────────────────┴──┘
                           │
                           ▼
         ┌──┬─────────────────────────┬──┐
         │  │     Call Fugacity       │  │
         │  │  (Calculate Fugacity)   │  │
         └──┴─────────────────────────┴──┘
                           │
                           ▼
          ╱───────────────────────╱
         ╱  Print φ^l, φ^v,      ╱
        ╱   f^l and f^v         ╱
       ╱───────────────────────╱
                           │
                           ▼
                    ╭──────────────╮
                    │    STOP      │
                    ╰──────────────╯
```
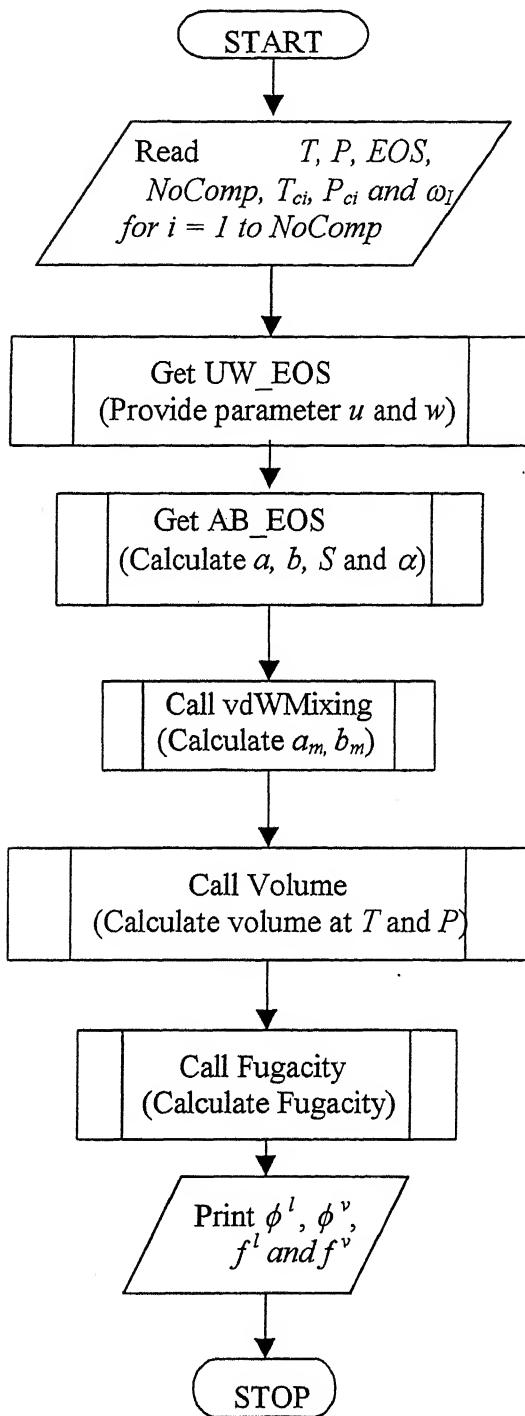
Fig. 3.9 *Flowchart for fugacity calculation of multi-component mixture*

Flowchart for the calculation of partial fugacity of a component in the Mixture

```
                    ( START )
                        |
                        v
       / Read      T, P, EOS,          /
      / NoComp, T_ci, P_ci and ω_i    /
     / for i = 1 to NoComp           /
                        |
                        v
    |  |      Get UW_EOS            |  |
    |  | (Provide parameter u and w) |  |
                        |
                        v
    |  |      Get AB_EOS            |  |
    |  | (Calculate a, b, S and α)  |  |
                        |
                        v
    |  |      Call vdWMixing        |  |
    |  |   (Calculate a_m, b_m)     |  |
                        |
                        v
    |  |       Call Volume          |  |
    |  |   (Calculate volume)       |  |
                        |
                        v
    |  |   Call Partial_Fugacity    |  |
    |  | (Calculate f̂_i^l and f̂_i^v) |  |
                        |
                        v
         / Print φ_i^l, φ_i^v,     /
        / f̂_i^l and f̂_i^v         /
                        |
                        v
                    ( STOP )
```
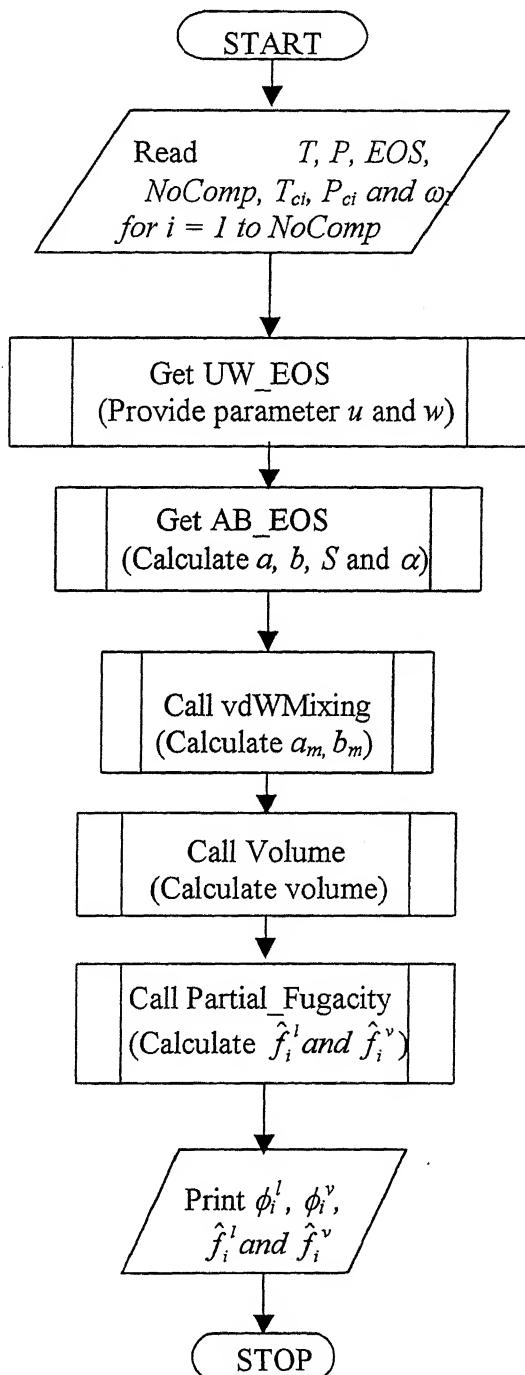
Fig. 3.10 *Flowchart for partial fugacity calculation of a component in a multi-component mixture*

Flowchart for the calculation of bubble point pressure

START

Read EOS, T, NoComp, x_i's, P_{ci}'s, T_{ci}'s, ω_i's

Call sat_P

Guess bubble P
$$P = \Sigma x_i P_i^{sat}$$

Guess value of K_i
$$K_i = P_i^{sat} / P$$

Calculate $y_i = K_i x_i$

Call Partial_Fugacity

Calculate $y_i = \dfrac{\phi_i^{l}}{\phi_i^{v}} x_i$

B

B

Is $y_i' = y_i$? — No → Set $y_i = y_i'$

Yes

Is $\Sigma y_i' = 1$? — No → Revise bubble P $P = P\Sigma y_i'$

Yes

Print P, y_i's

STOP
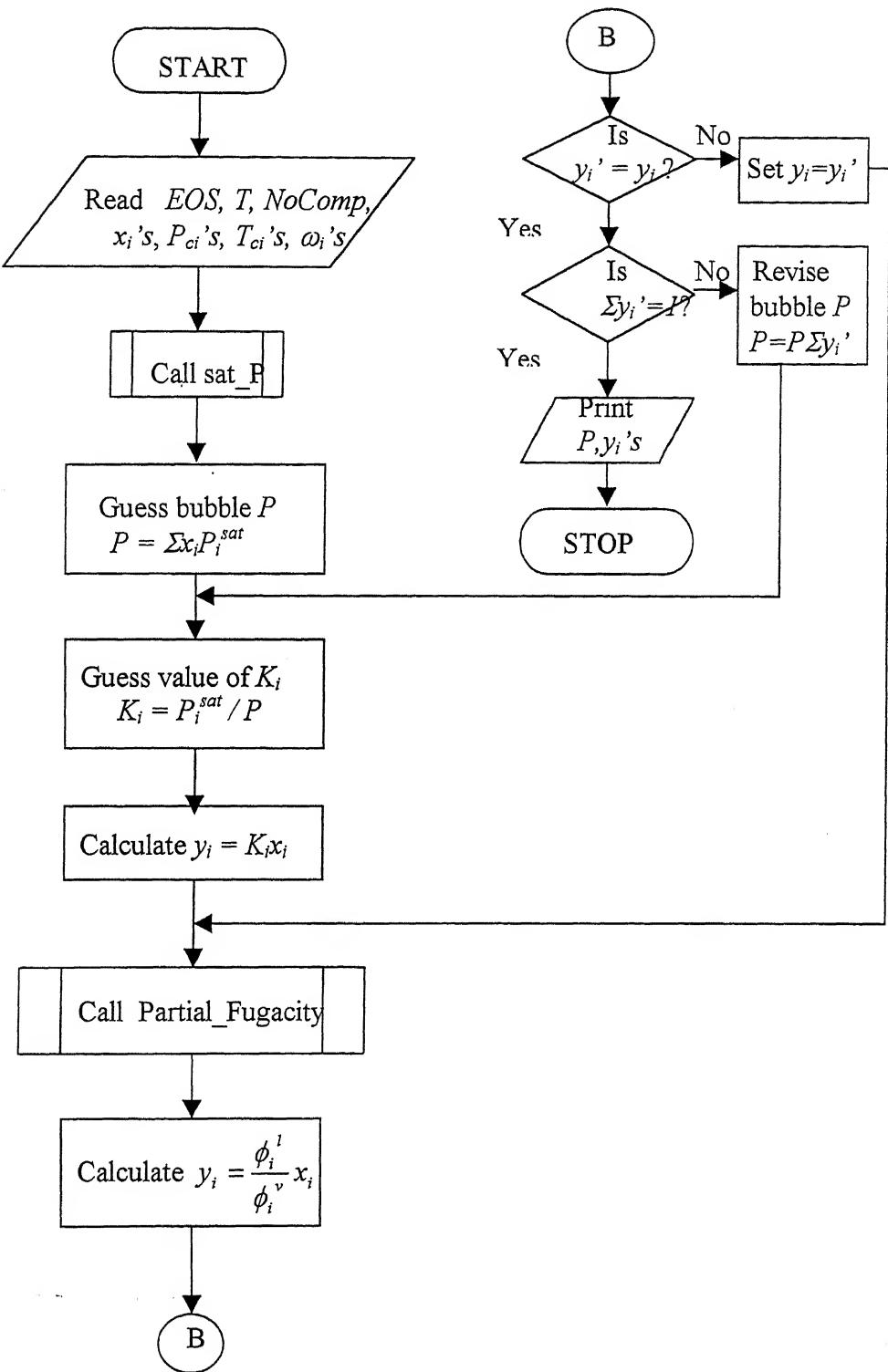
Fig. 3.11 *Flowchart for bubble point pressure calculation*

Flowchart for the calculation of bubble point temperature

START

Read   EOS, P, NoComp, x_i's, P_{ci}'s, T_{ci}'s, ω_i's

Call Sat_T

Guess bubble T
$T = \Sigma x_i T_i^{sat}$

Call Sat_P

Guess value of K_i
$K_i = P_i^{sat} / P$

Calculate $y_i = K_i x_i$

Call Partial_Fugacity

Calculate $y_i = \dfrac{\phi_i^l}{\phi_i^v} x_i$

C

C

Is $y_i' = y_i$?   No   Set $y_i = y_i'$

Yes

Is $\Sigma y_i' = 1$?   No   Revise bubble T

Yes

Print T, y_i's

STOP
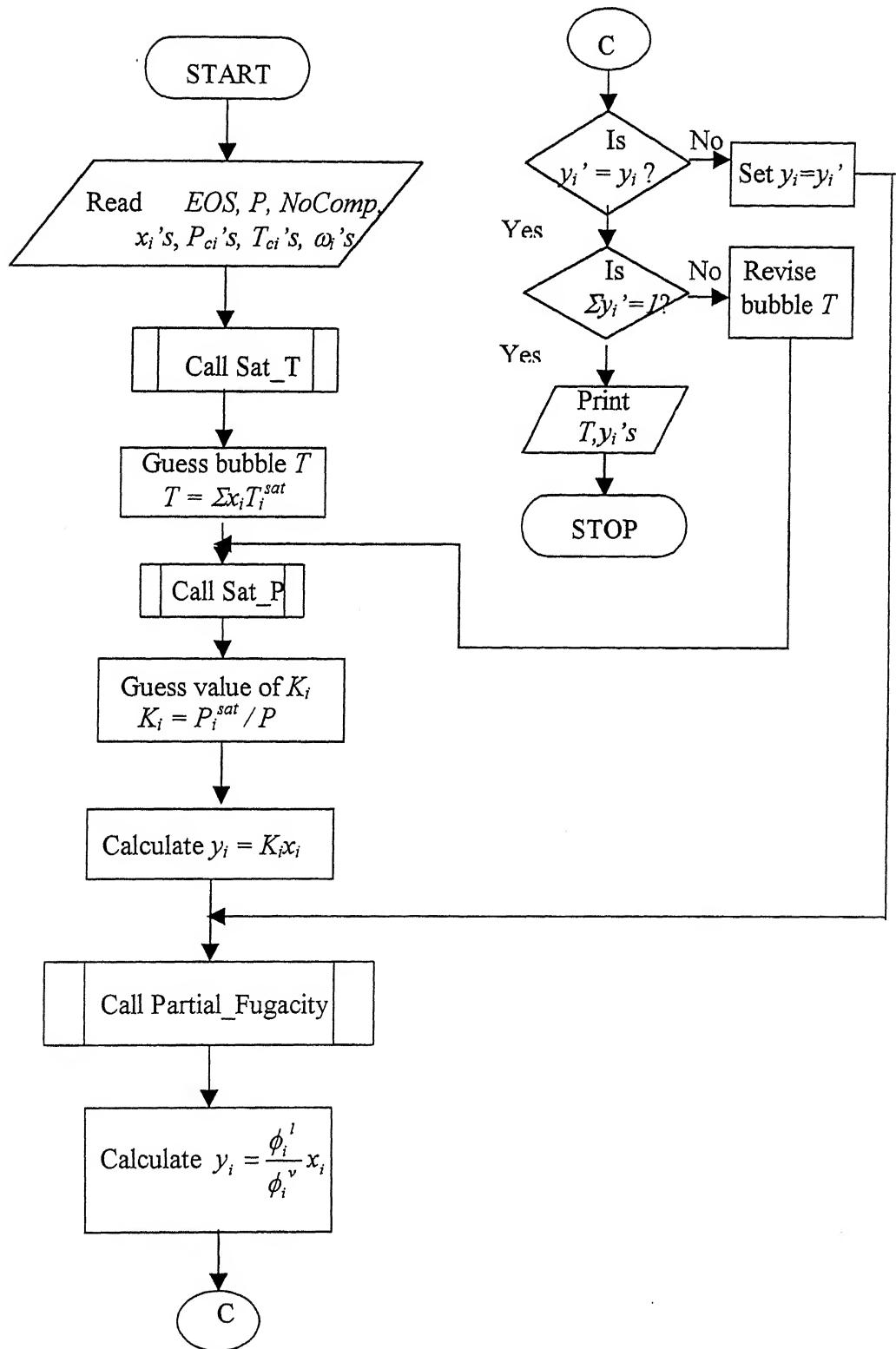
Fig. 3.12 *Flowchart for bubble point temperature calculation*

Flowchart for the calculation of Dew point temperature

START

Read *EOS, P, NoComp, x_i's, P_{ci}'s, T_{ci}'s, ω_i's*

Call Sat_T

Guess Dew T
$T = \Sigma y_i T_i^{sat}$

Call Sat_P

Guess value of K_i
$K_i = P_i^{sat} / P$

Calculate $x_i = y_i / K_i$

Call Partial_Fugacity

Calculate $x_i = \dfrac{\phi_i^{v}}{\phi_i^{l}} y_i$

D

D

Is $x_i' = x_i$? — No → Set $x_i = x_i'$

Yes

Is $\Sigma x_i' = 1$? — No → Revise Dew T

Yes

Print T, x_i's

STOP
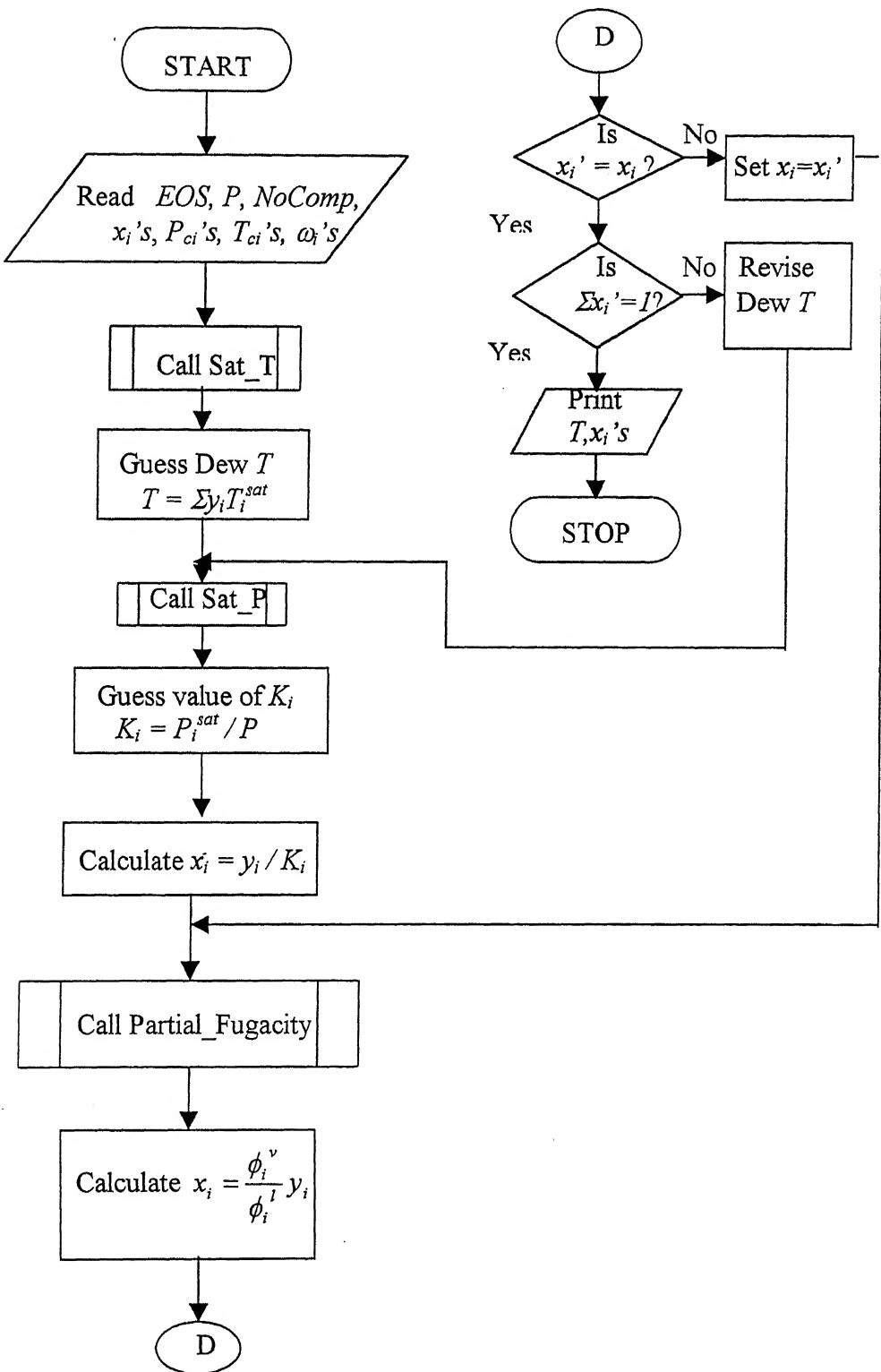
Fig 3.13 *Flowchart for Dew point temperature calculation*

Flowchart for the calculation of Dew point pressure

START

Read *EOS, T, NoComp,* x_i's, P_{ci}'s, T_{ci}'s, ω_i's

Call Sat_P
(Calculate saturation pressure at *T*)

Guess Dew *P*
$P = \Sigma y_i P_i^{sat}$

Guess value of K_i
$K_i = P_i^{sat} / P$

Calculate $x_i = y_i / K_i$

Call Partial_Fugacity

Calculate $x_i = \dfrac{\phi_i^{v}}{\phi_i^{l}} y_i$

E

E

Is $x_i' = x_i$? — No → Set $x_i = x_i'$

Yes

Is $\Sigma x_i' = 1$? — No → Revise Dew *P* $P = P / \Sigma x_i'$

Yes

Print *T,* x_i's

STOP
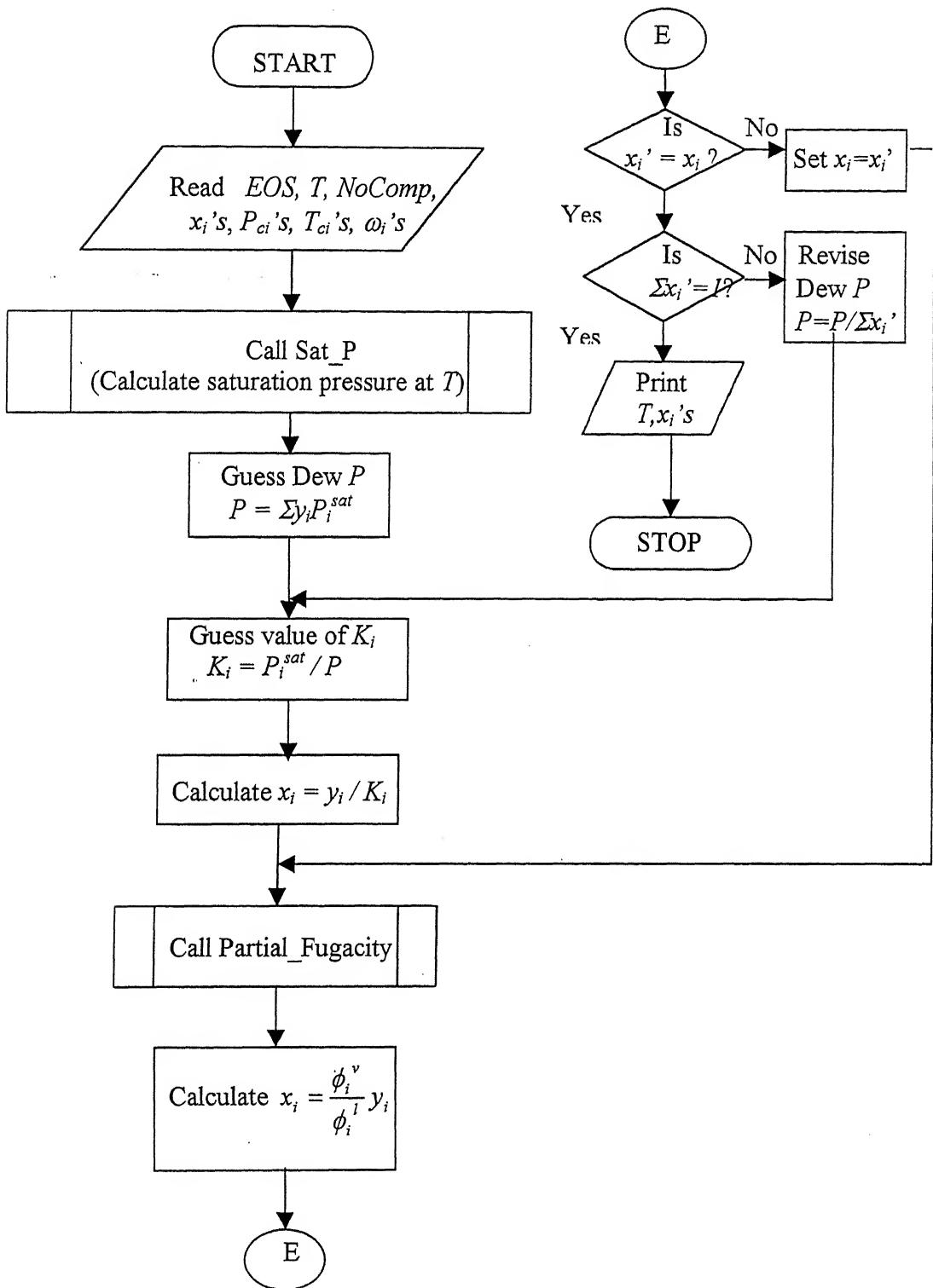
Fig. 3.14 *Flowchart for Dew point pressure calculation*

Flowchart for the calculation of T-x-y data

START

Read P, EOS, x_i's, T_{ci}, P_{ci} and ωi for both the components.

Call Sat_T
(Calculate Saturation temperature at P)

Calculate Guess T
$$T = \Sigma x_i T_i^{sat}$$

Calculate activity coefficients using any one of the following subroutines
Wilson \ vanLaar \ Margules \ NRTL or UNIFAC

Call Sat_P
(Calculate saturation pressure at T)

Calculate $y_i = \dfrac{\gamma_i x_i P_i^{sat}}{P}$ for $i = 1$ and 2

Revise
$T = T + h$

< 1

Is
Σy

> 1

Revise
$h=h/10$
$T = T - h$

$= 1$

Print
T, x, y

STOP

Fig. 3.15 *Flowchart for VLE calculation*

Subroutine Get_UW_EOS

```
        ┌─────────────┐
        │ Input data: │
        │    EOS      │
        └─────────────┘
               │
               ▼
```

Is EOS = 1 → Yes → Set u = 0, w = 0

No

Is EOS = 2 → Yes → Set u = 1, w = 0

No

Is EOS = 3 → Yes → Set u = 1, w = 0

No

Is EOS = 4 → Yes → Set u = 2, w = -1

No

Message: EOS not valid

Return
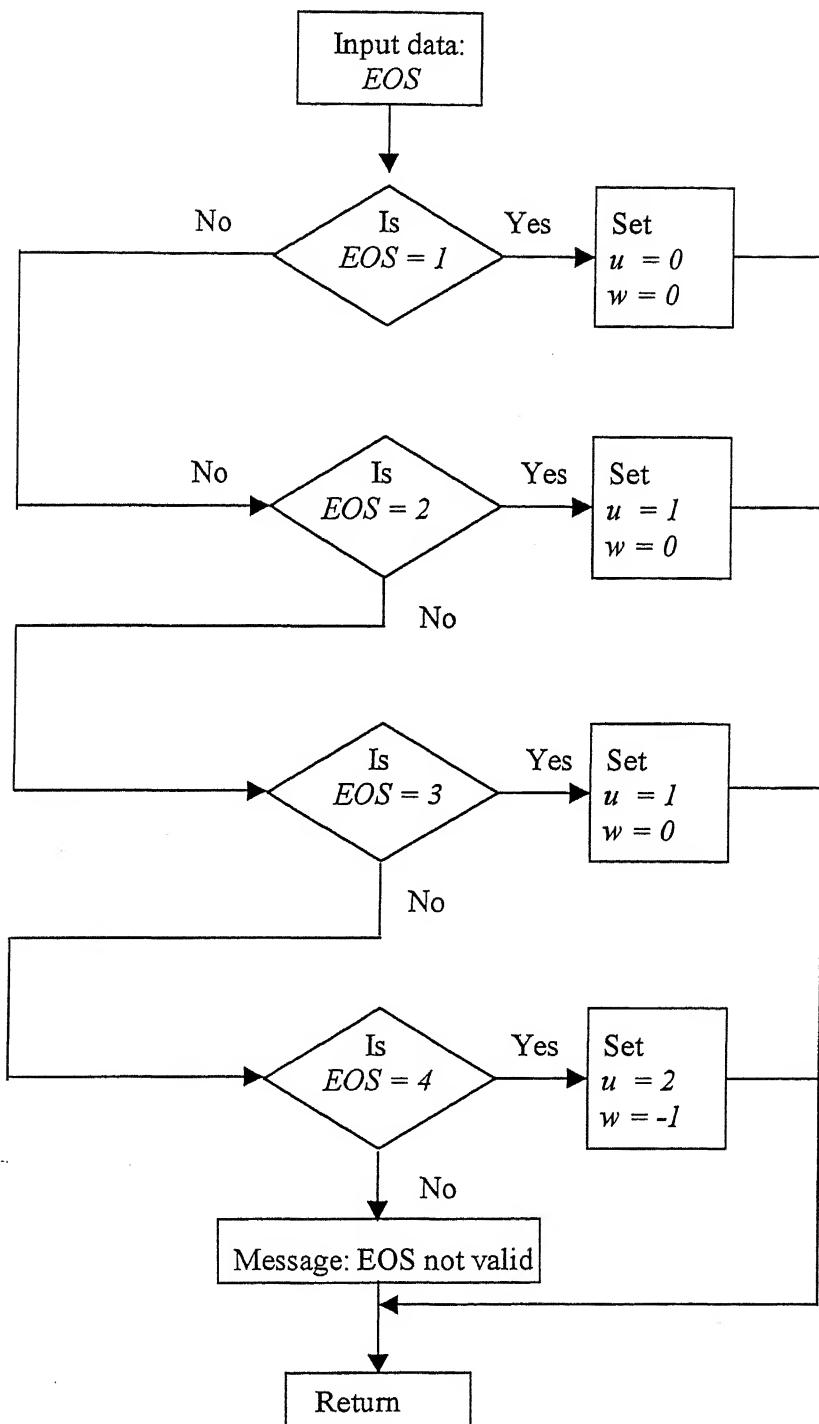
Fig. 3.16 *Subroutine for u and w*

Subroutine Get_AB_EOS

Fig. 3.17 *Subroutine for EOS parameter*

Subroutine Get_AB_EOS

Input data:
EOS, T, T_C and P_C

Is $EOS = 1$ — No / Yes

Calculate
$$a = \frac{27R^2T_C^2}{64P_C}$$
$$b = \frac{RT_C}{8P_C}$$

Is $EOS = 2$ — No / Yes

Calculate
$$a = 0.42748\frac{R^2T_C^{2.5}}{P_C}$$
$$b = 0.08664\frac{RT_C}{P_C}$$

Is $EOS = 3$ — No / Yes

Calculate
$$S = 0.48 + 1.574\omega - 0.176\omega^2$$
$$\sqrt{\alpha} = 1 + S\left(1 - \sqrt{T_r}\right)$$
$$a = 0.42748\frac{R^2T_C^2\alpha}{P_C}$$
$$b = 0.08664\frac{RT_C}{P_C}$$

Calculate
$$S = 0.37464 + 1.5426\omega - 0.269\omega^2$$
$$\sqrt{\alpha} = 1 + S\left(1 - \sqrt{T_r}\right)$$
$$a = 0.45724\frac{R^2T_C^2\alpha}{P_C}$$
$$b = 0.07780\frac{RT_C}{P_C}$$

Return

Fig. 3.17 *Subroutine for EOS parameter*

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Subroutine Volume

Input data:
$A, B, \alpha, b, u,$ and w

Calculate
$A = aP/(RT)^2$ $B = bP/RT$
$\alpha = -1 - B + u$ $\beta = A + \omega B^2 - uB - uB^2$
$\gamma = -AB - \omega B^2 - \omega B^3$
$p = \beta - (\alpha^2/3)$
$q = (2\alpha^3/27) - (\alpha\beta/3) + \gamma$
$D = (q^2/4) + (p^3/27)$

$D > 0$ Check the status Of D $D < 0$

$D = 0$

There is only one real root

$$Z = \left\{-\frac{q}{2} + \sqrt{D}\right\}^{1/3} + \left\{-\frac{q}{2} - \sqrt{D}\right\}^{1/3} - \frac{\alpha}{3}$$

There are three real roots and Two of them are equal.

$$Z_1 = -2\left(\frac{q}{2}\right)^{1/3} - \frac{\alpha}{3}$$

$$Z_2 = Z_3 = \left(\frac{q}{2}\right)^{1/3} - \frac{\alpha}{3}$$

There are three unequal Real roots

$$Z_1 = 2r^{1/3}\cos\left(\frac{\theta}{3}\right) - \frac{\alpha}{3}$$

$$Z_2 = 2r^{1/3}\cos\left(\frac{2\pi + \theta}{3}\right) - \frac{\alpha}{3}$$

$$Z_3 = 2r^{1/3}\cos\left(\frac{4\pi + \theta}{3}\right) - \frac{\alpha}{3}$$

$$where \quad \cos\theta = -\frac{q}{2}\left(\frac{-27}{p^3}\right)^{1/2}$$

$$r = \left(\frac{p^3}{-27}\right)^{1/2}$$

If more then one value of Z's are available, they are compared and highest value of Z is taken as Z_v and lowest of them is taken as Z_l

$v_v = Z_v RT/P$ $v_l = Z_l RT/P$

Return

Fig. 3.18 *Subroutine for volume calculation*

Subroutine Enthalpy Departure

Input data:
EOS, A, B, a, b, T_c, P_c, and T

Depending upon the choice of the equation of state appropriate equations given in *section 2. 2.2* are used. Equations for PR EOS are

$$\left(\frac{\partial a}{\partial T}\right) = -\frac{0.45724R^2T_c^{\,2}S}{P_c}\sqrt{\frac{\alpha}{TT_c}}$$

$$(h-h^0)_{T,P} = RT(Z-1) + \frac{T\left(\frac{\partial a}{\partial T}\right)-a}{2\sqrt{2}b}\ln\left(\frac{Z+B\left(1+\sqrt{2}\right)}{Z+B\left(1-\sqrt{2}\right)}\right)$$

Return
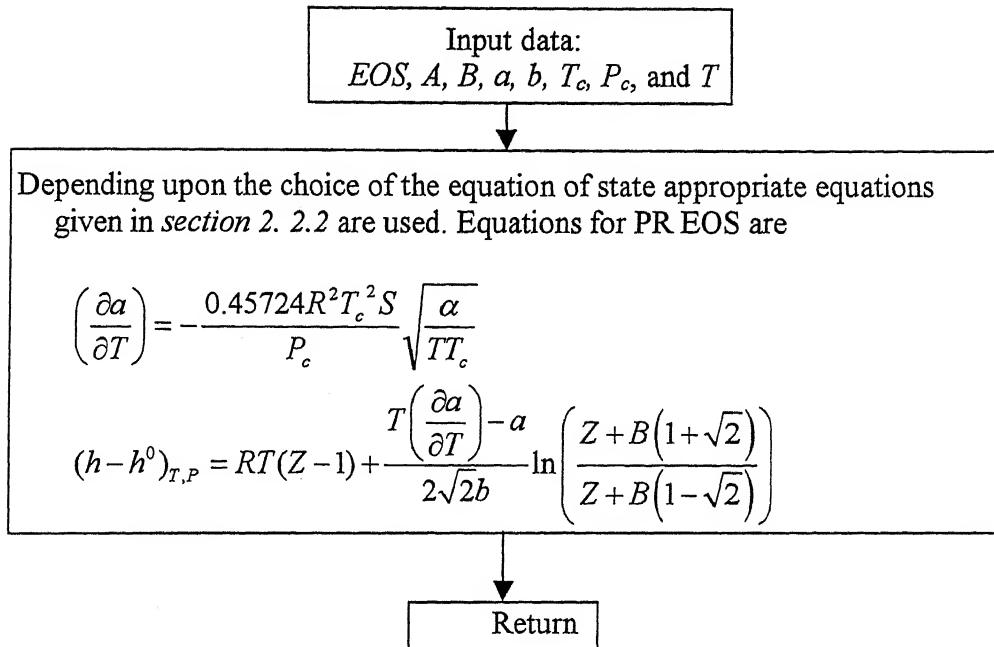
Fig. 3.19 *Subroutine for enthalpy departure calculation*

Subroutine Entropy Departure

Input data:
EOS, A, B, a, b, T_c, P_c, and T

Depending upon the choice of the equation of state appropriate equations given in *section 2. 2.2* are used. Equations for PR EOS are

$$\left(\frac{\partial a}{\partial T}\right) = -\frac{0.45724R^2T_c^{\,2}S}{P_c}\sqrt{\frac{\alpha}{TT_c}}$$

$$(s-s^0)_{T,P} = R\ln(Z-B) + \frac{1}{2\sqrt{2}b}\left(\frac{\partial a}{\partial T}\right)\ln\left(\frac{Z+B\left(1+\sqrt{2}\right)}{Z+B\left(1-\sqrt{2}\right)}\right)$$

Return
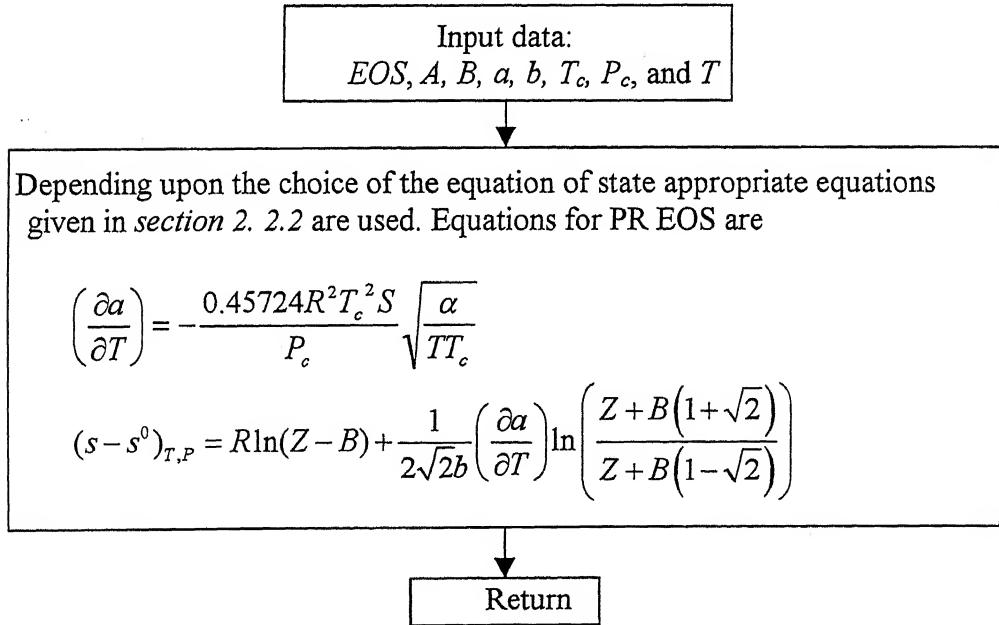
Fig. 3.20 *Subroutine for Entropy departure calculation*

Subroutine Fugacity

Input data:
$EOS, A, B, a, b, T_c, P_c,$ and T

Depending upon the choice of the equation of state appropriate equations given in *section 2. 2.3* are used. Equations for PR EOS are

$$\phi = Z - 1 - \ln(Z - B) - \frac{a}{2\sqrt{2}bRT}\ln\left(\frac{Z + B\left(1 + \sqrt{2}\right)}{Z + B\left(1 - \sqrt{2}\right)}\right)$$

$$\phi = Z - 1 - \ln(Z - B) - \frac{a}{2\sqrt{2}bRT}\ln\left(\frac{Z + B\left(1 + \sqrt{2}\right)}{Z + B\left(1 - \sqrt{2}\right)}\right)$$

Calculate $f = \phi \times P$

Return
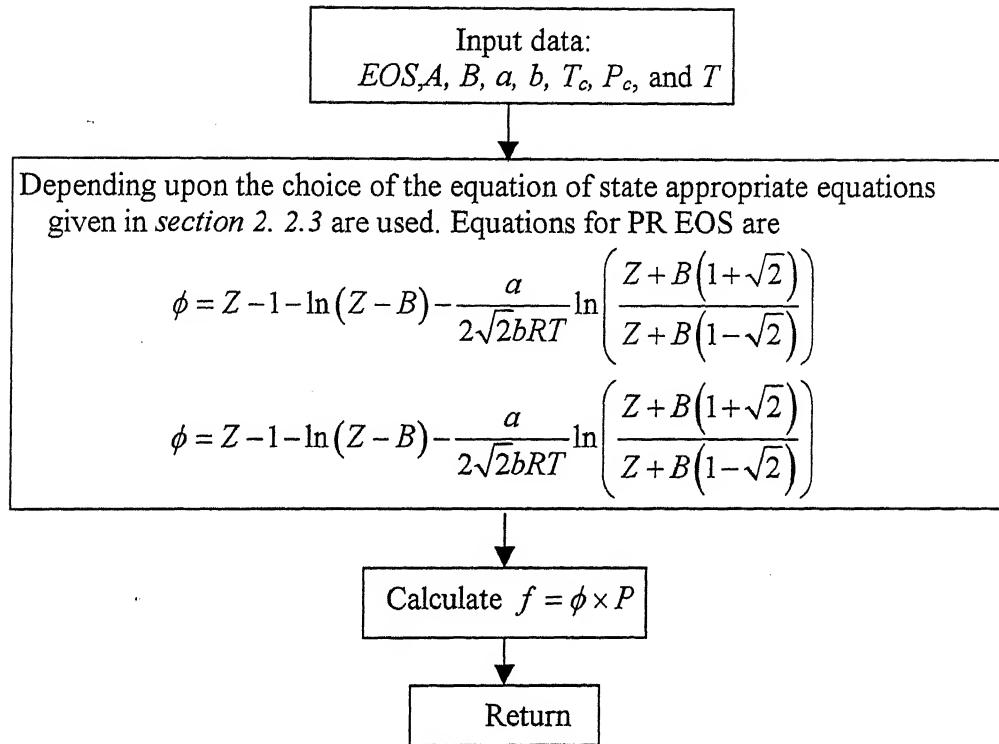
Fig. 3.21 *Subroutine for fugacity calculation*

Subroutine Watson

Input data:
T_c, P_c, T_{NBP} and T

Calculate Enthalpy of vaporization at *NBP*

$$T_{br} = \frac{T_{NBP}}{T_c}$$

$$\Delta h_{vn} = 1.093RT\left[T_{br}\frac{\ln P_c - 1.013}{0.930 - T_{br}}\right]$$

F
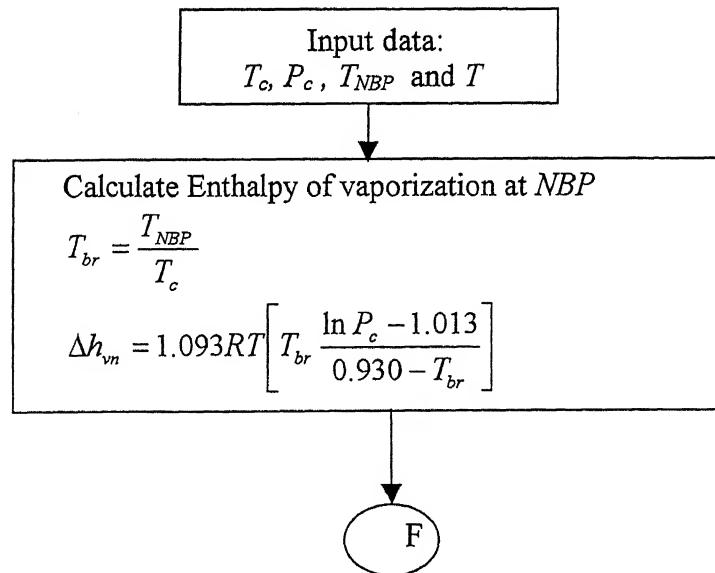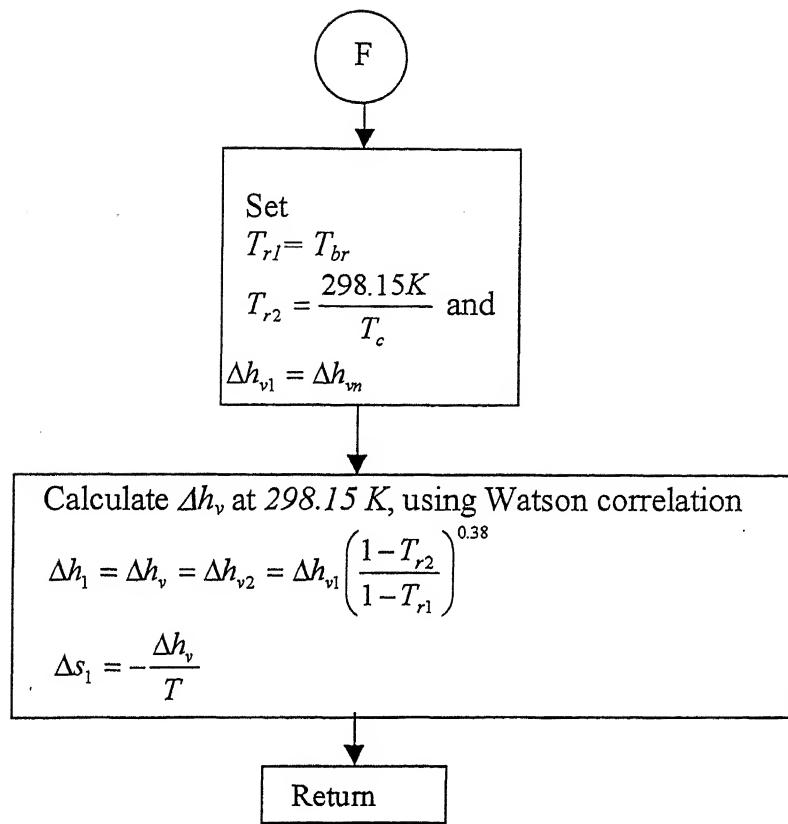
Fig. 3.22 *Subroutine for Watson correlation*

Subroutine NTPNTH_IDL

Input data:

$P^{sat}_{298.15}$, T, P and $C^{o}{}_{p}$ equation constants

Calculate Enthalpy and entropy change

$$\Delta h = \int_{T1}^{T2} C^{o}{}_{p} dT$$

$$\Delta s = \int_{T1}^{T2} C^{o}{}_{p} dT - R \ln \frac{P_2}{P_1}$$

Return
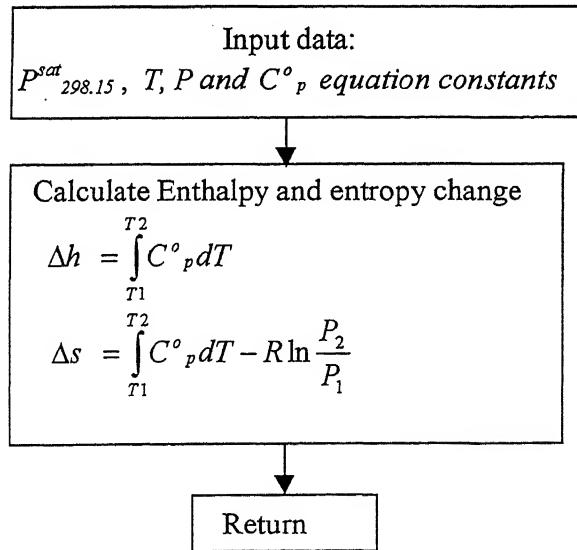
Fig. 3.23 *Subroutine for enthalpy change for ideal gas*

Subroutine vdWMixing

Input data:
$NoComp$, a_i's, b_i's and y_i's

Calculate Mixture parameter using vdW Mixing rule
Set all $K_{ij} = 0$

$$a_m = \sum_{i,j} y_i y_j \sqrt{a_i a_j}$$

$$b_m = \sum_i y_i b_i$$

Return
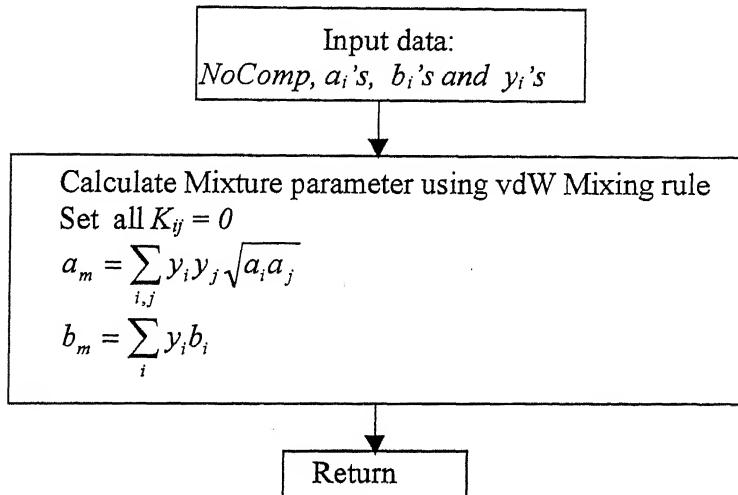
Fig. 3.24 *Subroutine for vdW Mixing rule*

Subroutine Partial_Fugacity

Input data:
EOS, $NoComp$, a_i's, b_i's, y_i's A, B, Z, a_m, b_m, T_{ci}'s, P_{ci}'s, P and T

Depending upon the choice of the equation of state appropriate equations given in *section 2. 3.1* are used. Equations for PR EOS are

$$\frac{b_i}{b} = \frac{\left(\dfrac{T_{ci}}{P_{ci}}\right)}{\sum_i \left(\dfrac{y_i T_{ci}}{P_{ci}}\right)}$$

$$\ln \hat{\phi}_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) + \frac{a}{2\sqrt{2}RT}\left[\frac{b_i}{b} - 2\sqrt{\frac{a_i}{a}}\right]\ln\left[\frac{Z+B(1+\sqrt{2})}{Z+B(1-\sqrt{2})}\right]$$

Calculate $\hat{f}_i = \hat{\phi}_i \times y_i \times P$ for all i

Return
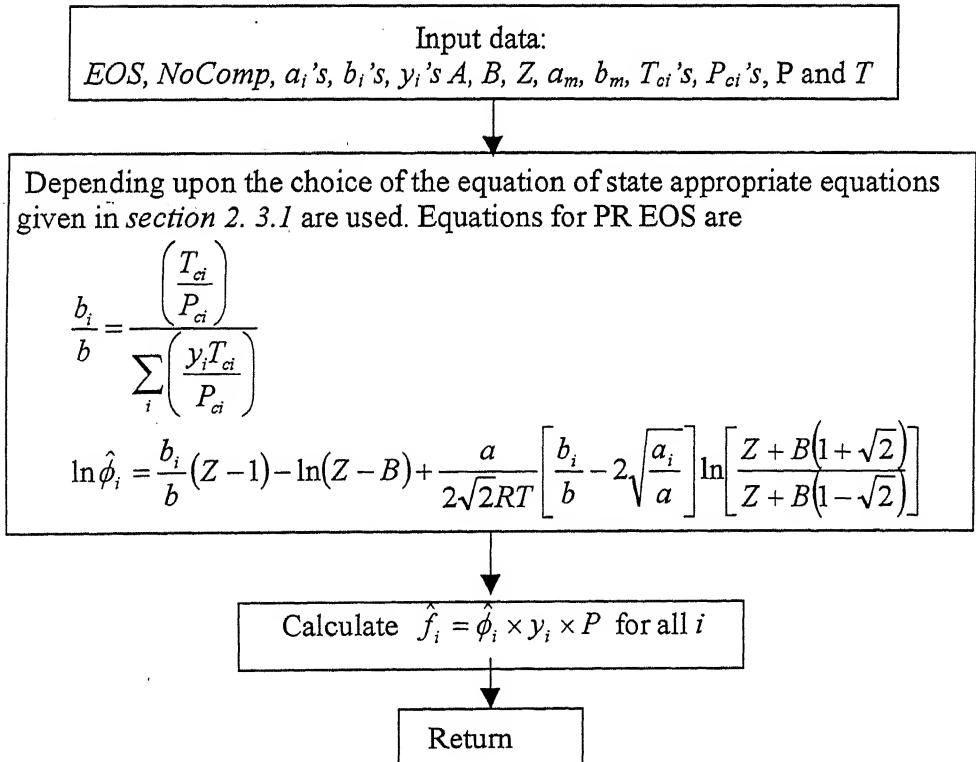
Fig. 3.25 *Subroutine for Partial fugacity*

Subroutine Margules
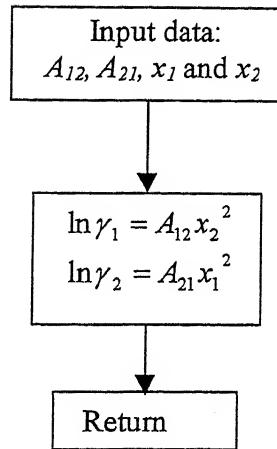
Fig. 3.26 *Subroutine for Margules Equation*

Subroutine vanLaar
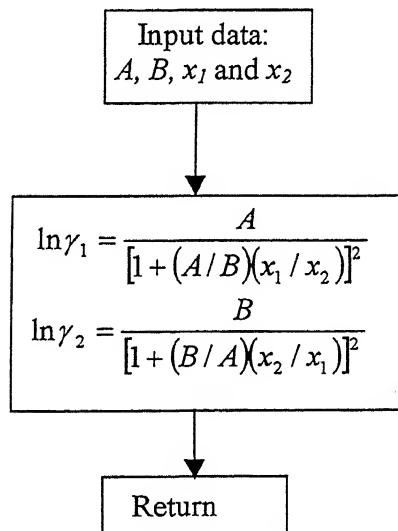
Fig. 3.27 *Subroutine for van Laar Equation*

Subroutine Wilson

$$\boxed{\begin{array}{l} \text{Input data:} \\ V_{12},\ V_{21},\ x_1 \text{ and } x_2 \end{array}}$$

$$\ln\gamma_1 = -\ln(x_1 + V_{12}x_2) + x_2\left\{\frac{V_{12}}{x_1 + V_{12}x_2} - \frac{V_{21}}{x_1 + V_{21}x_2}\right\}$$

$$\ln\gamma_2 = -\ln(x_2 + V_{21}x_1) + x_2\left\{\frac{V_{12}}{x_1 + V_{12}x_2} - \frac{V_{21}}{x_1 + V_{21}x_2}\right\}$$

Return
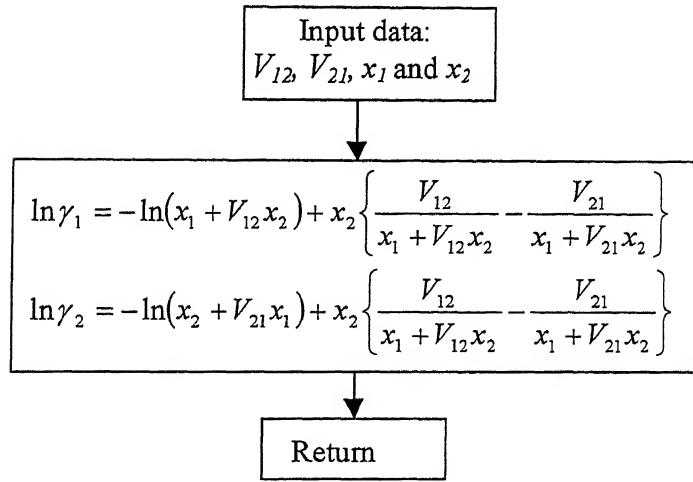
Fig. 3.28 *Subroutine for Wilson Equation*

Subroutine NRTL

$$\begin{array}{l} \text{Input data:} \\ g_{12} - g_{22},\ g_{21} - g_{11},\ \alpha_{12},\ x_1 \text{ and } x_2 \end{array}$$

$$\tau_{12} = (g_{12} - g_{22})/RT$$

$$\tau_{21} = (g_{21} - g_{11})/RT$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12})$$

$$G_{21} = \exp(-\alpha_{12}\tau_{21})$$

$$\ln\gamma_1 = x_2^{\,2}\left[\tau_{21}\left\{\frac{G_{21}}{x_1 + x_2 G_{21}}\right\}^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1 G_{12})^2}\right]$$

$$\ln\gamma_2 = x_1^{\,2}\left[\tau_{12}\left\{\frac{G_{12}}{x_2 + x_1 G_{12}}\right\}^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2 G_{21})^2}\right]$$

Return
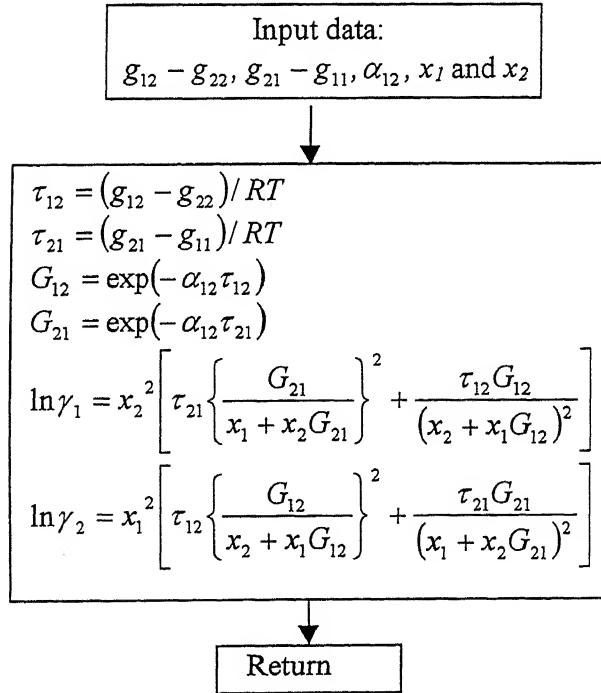
Fig. 3.29 *Subroutine for NRTL Equation*

Subroutine UNIFAC

Input data:
R_k, Q_k, a_{mn}'s , x_1, x_2 and T

Calculate for i = 1 and 2

$$q_i = \sum_k \nu_k^{(i)} Q_k$$

$$r_i = \sum_k \nu_k^{(i)} R_k$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}$$

$$\psi_{mn} = \exp\left(-\frac{u_{mn} - un}{RT}\right) = \exp\left(-\frac{a_{mn}}{T}\right)$$

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \theta_m \psi_{mk}\right) - \sum_m \frac{\theta_m \psi_{mk}}{\sum_n \theta_m \psi_{nm}}\right]$$

$$\ln \gamma_i^R = \sum \nu_k^{(i)} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)}\right)$$

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j$$

Calculate $\gamma_i = \gamma_i^C + \gamma_i^R$ for $i = 1$ and 2

Return
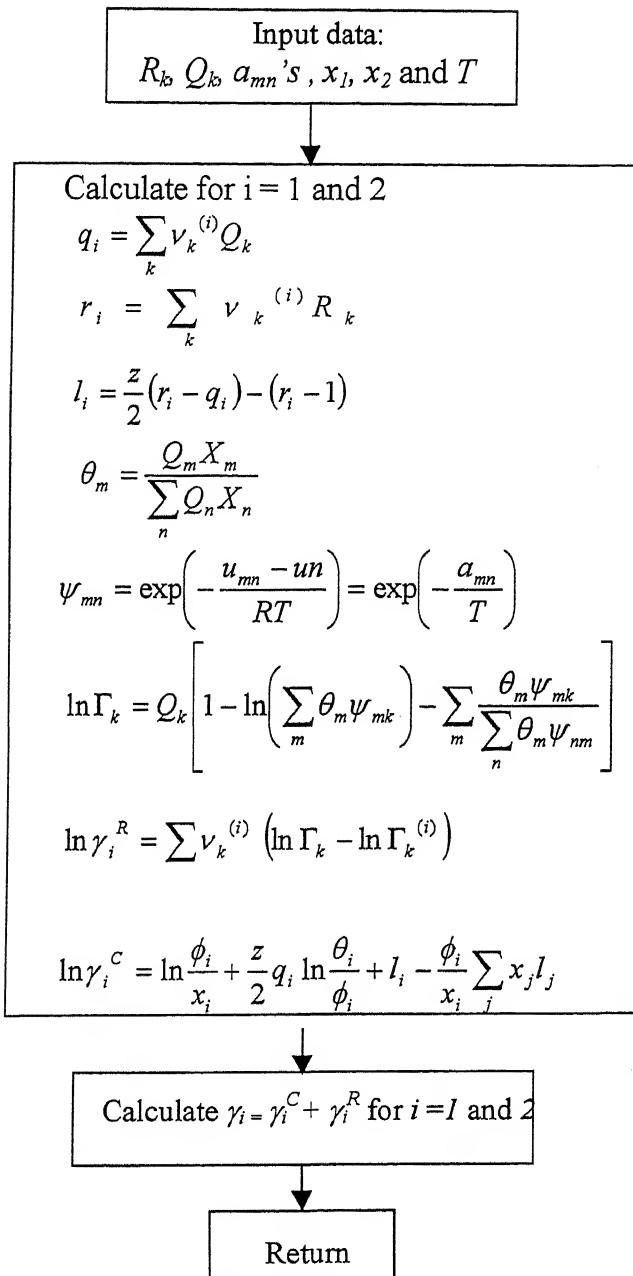
Fig. 3.30 *Subroutine for UNIFAC Equation*

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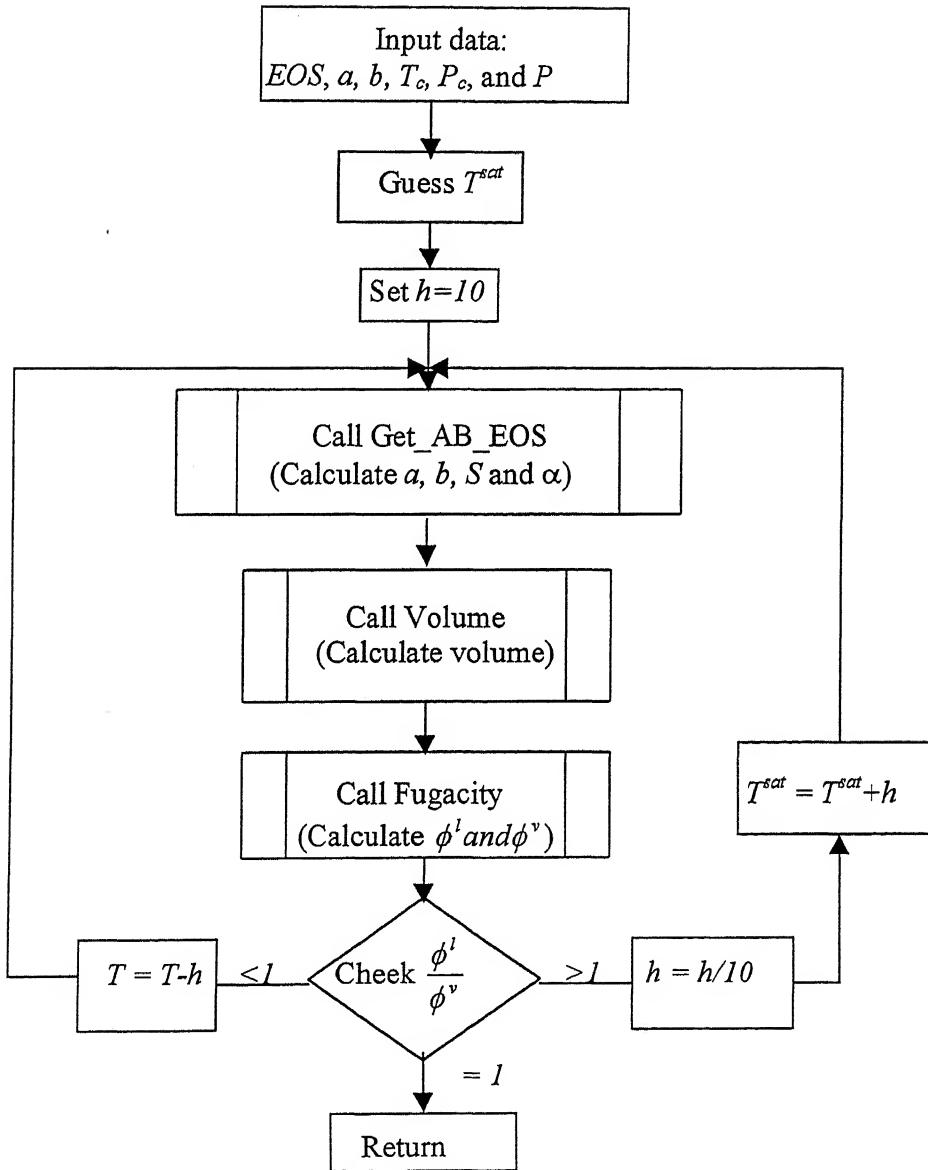
Subroutine Sat_T

Fig. 3.31 *Subroutine sat_T*

Subroutine Sat_P

Input data:
EOS, a, b, T_c, P_c, and T

Guess P^{sat}

Call Volume
(Calculate volume)

Call Fugacity
(Calculate ϕ^l and ϕ^v)

Is $\phi^l = \phi^v$

No → $P^{sat} = \dfrac{\phi^l}{\phi^v} P^{sat}$

Yes

Return
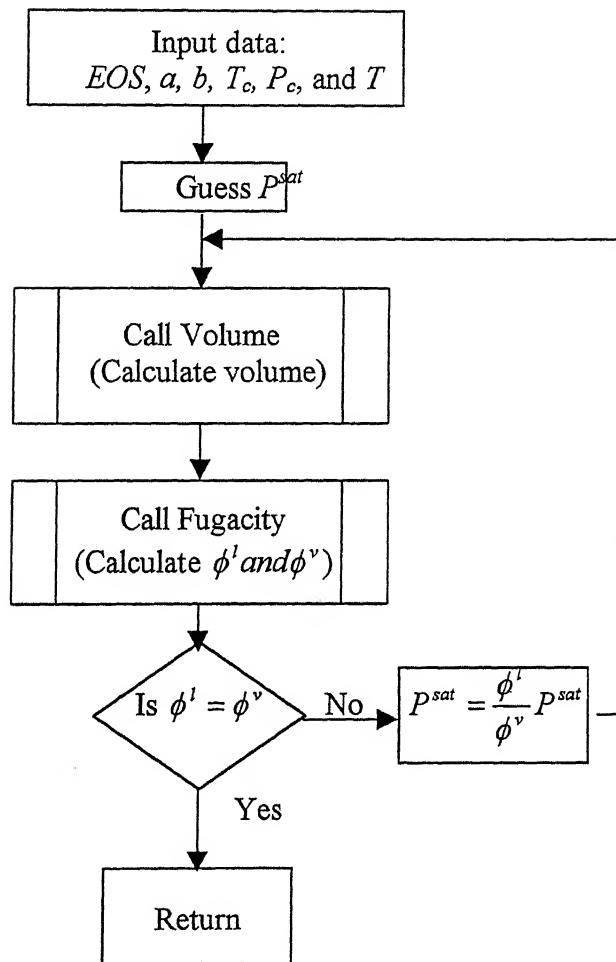
Fig. 3.32 *Subroutine sat_P*

Chapter 4

SAMPLE INPUT / OUTPUT

In this chapter, sample input/output is provided for each of the thermodynamic properties that can be predicted by the software. As the input windows are same for almost all the properties, to avoid the repetition the input windows are shown for volume calculation only. For the rest of the properties only the output window is provided which contains input as well as output information.

4.1 Sample Input/Output For Volume Calculation

Here is a sample input/output for the calculation of pure component volume using cubic equation of state. The first window that appears is shown below.

Main Window

Volume Calculation using Cubic EOS

Volume Calculation

About Cardan's Method
Set Units for T, P, & V
Run Volume Calculator
Quit

Press Enter to Select   Arrow key to Move
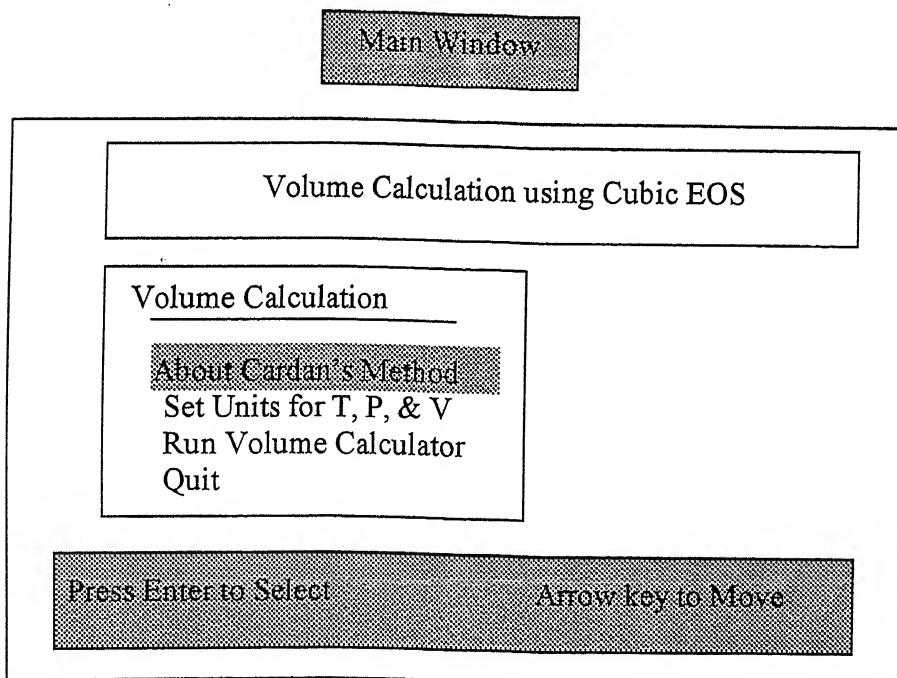
When user selects *Run volume calculator* and presses the *ENTER* Key the following input window will appear in which the user enters the values shown in italics.

VOLUME CALCULATION USING EOS

The CARDAN'S Method will be used To Solve Cubic EOS. This method allows direct solution of any cubic Equation Of State. The following four cubic EOS can be selected.

1. van der Walls (VDW)   2. Redlich Kwong (RK)
3. Soave Redlich Kwong (SRK)   and   4. Peng Robinson (PR) EOS.

Enter the Temperature of the Fluid in K   : 427.98

Enter the Acentric Factor 'w'   : 0.398

Type of Equation to use? VDW/RK/PR/SRK   : PR

F1(Calculate)   ESC (Quit)

When user presses *F1* Key after entering the above data, new Window will appear asking for the name of substance for which calculation is to be done.

Enter The Name of the Substance: *N-OCTANE*

This completes the required input for the program and the output window will appear as shown below.

Volume Calculations using PENG ROBINSON equation of state

Input Data:

Compound Name: N-OCTANE
Critical Temperature = 569.8 K   Critical Pressure = 24.970 BAR
Temperature   = 428.0 K   Pressure   = 2.150 BAR
Acentric Factor   = 0.3980

All the Calculations were done in the following units
Temperature in Kelvin   Pressure in Pascal   Volume in m3/mol.

Input Data (After Conversion)

Critical Temperature = 569.8 Kelvin   Critical Pressure = 2497000 Pascal

Temperature   = 428.0 Kelvin   Pressure   = 215000 Pascal

Acentric Factor   = 0.398000

A = 0.088494   B = 0.008919

alpha = -0.991081   beta = 0.070418   gamma = -0.000709
p   = -0.256996   q   = -0.049555   D   = -0.000015

The value of theta is 0.153645
Vg = 1.514e-02 cubic meter/mol
Vl = 2.003e-04 cubic meter/mol

RESULTS:

Vg(per mole) = 15.143 LITERS
Vl(per mole) = 0.200 LITERS

The Volume calculator can give *P-v* as well as *T-v diagram* for which the user will provide temperature and pressure range. Following is a *P-v diagram* for *T= 450.0 Kelvin* and for the pressure range of *1.0 bar* to *6.0 bar*.
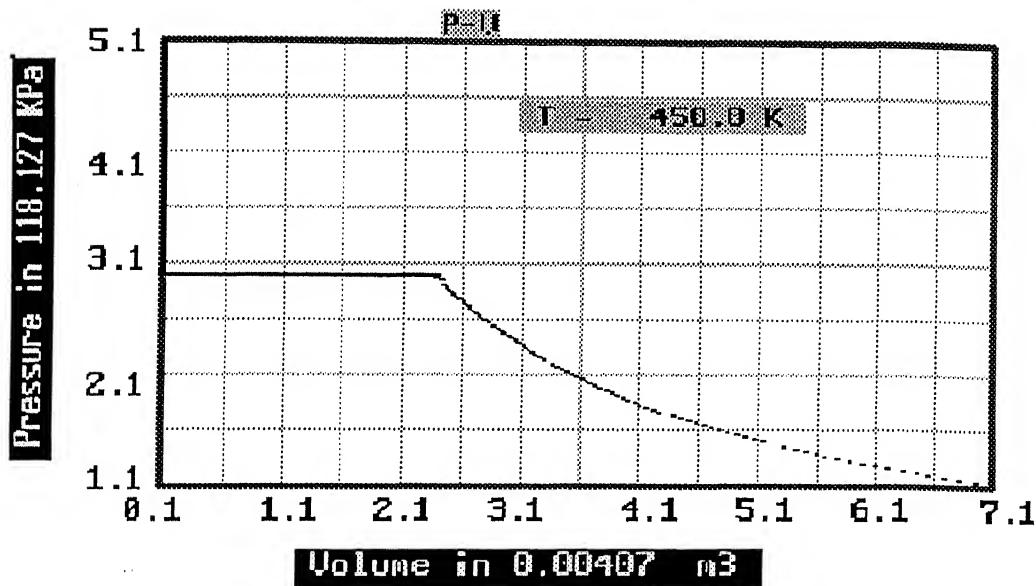
Fig. 4.1. *Pressure vs. Molar volume diagram*

4.2 Sample Output For Enthalpy And Entropy Departure Calculation

Following is the output window, obtained by using the departure calculator to calculate enthalpy and entropy departure for *N-OCTANE* at *428.0 Kelvin* and *2.15 bar*.

Output Window

Departure Calculations for PENG ROBINSON equation of state
Input Data: Compound Name: N-OCTANE Critical Temperature = 569.8 K   Critical Pressure = 24.970 BAR Temperature   = 428.0 K   Pressure   = 2.150 BAR Acentric Factor   = 0.3980
Input Data (After Conversion) Critical Temperature = 569.8 Kelvin   Critical Pressure = 2497000 Pascal Temperature   = 428.0 Kelvin   Pressure   = 215000 Pascal Acentric Factor   = 0.398000

All the Calculations were done in the following units
Temperature in Kelvin   Pressure in Pascal   Volume in m3/mol.

A   = 0.088325   B   = 0.008912
Alpha = -0.991088   beta = 0.070262   gamma = -0.000707
p   = -0.257157   q   = -0.049606   D   = -0.000015

The value of theta is 0.153058
Vg = 1.515e-02 cubic meter/mol
Vl = 2.003e-04 cubic meter/mol

RESULTS:

dh(ENTHALPY DEPARTURE) = -0.8896 kJ/mol
ds(ENTROPY DEPARTURE) = -1.3973 J/mol.K

Q(Exit)   ESC(Quit to Main)   R(Run for New Data set)

The Departure calculator can give *departure function vs. pressure diagram* as well as *departure function* vs. *temperature diagram* for which the user will provide temperature and pressure ranges. The following *enthalpy departure vs. pressure diagram* and *entropy departure vs pressure diagram* are obtained by using departure calculator for *N-OCTANE* at *T= 427.0 Kelvin* and in the pressure range of *1.0 bar* to *10.0 bar*.
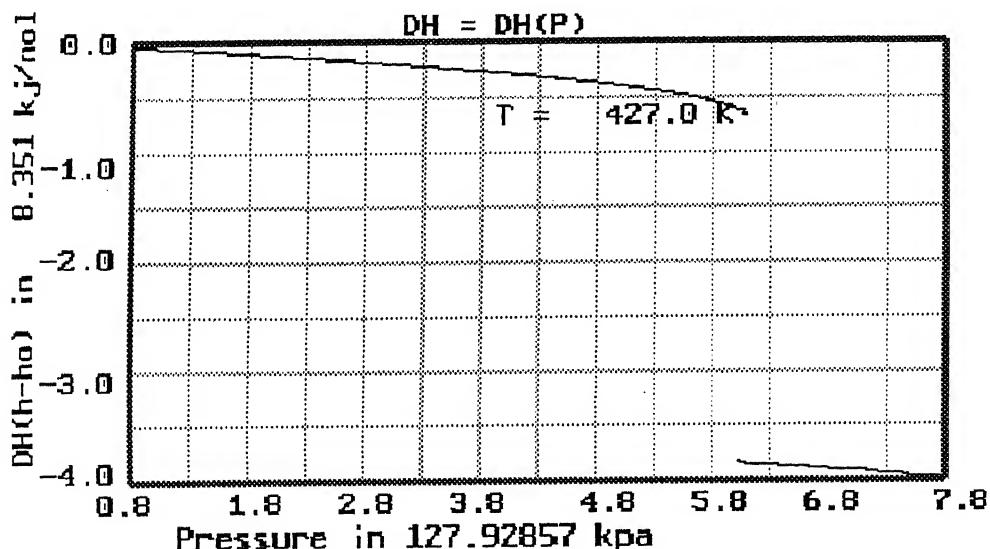
Fig. 4.2 *Enthalpy departure vs. pressure diagram*
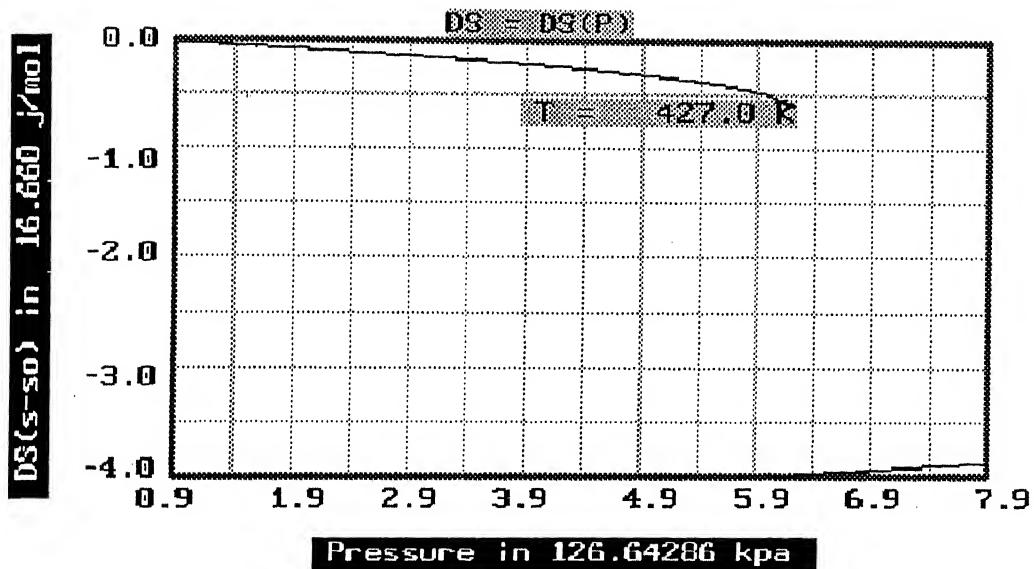
Fig. 4.3 *Entropy departure vs. pressure diagram*

4.3 Sample Output For Fugacity Calculation

The output window obtained by using the fugacity calculator for *N-OCTANE* at *427.98* Kelvin and *2.15* bar is shown below.

Output Window

Fugacity Calculations using PENG ROBINSON equation of state

Input Data:

Compound Name: N-OCTANE
Critical Temperature = 569.8 K   Critical Pressure = 24.970 BAR
Temperature = 428.0 K   Pressure = 2.150 BAR
Acentric Factor = 0.3980

All the Calculations were done in the following units
Temperature in Kelvin   Pressure in Pascal   Volume in m3/mol.

Input Data (After Conversion)

Critical Temperature = 569.8 Kelvin   Critical Pressure = 2497000 Pascal

Temperature = 428.0 Kelvin   Pressure = 215000 Pascal

Acentric Factor = 0.398000

```
A      = 0.088494        B      = 0.008919
alpha = -0.991081        beta = 0.070418         gamma = -0.000709
p      = -0.256996        q      = -0.049555       D         = -0.000015
```

The value of theta is 0.153058
Vg = 1.515e-02 cubic meter/mol
Vl = 2.003e-04 cubic meter/mol
Fugacity coefficient of liquid   =   0.909
Fugacity coefficient of vapor   =   0.921

RESULTS:

FUGACITY OF LIQUID   =   1.9552 BAR
FUGACITY OF VAPOR   =   1.9808 BAR

The fugacity calculator can give *fugacity coefficient vs. pressure* as well as *fugacity coefficient vs temperature diagram* for which the user will provide temperature and pressure range. Following is a *fugacity coefficient vs pressure diagram* for *T= 450.0 Kelvin* and for the pressure range of *1.0 bar* to *6.0 bar*.
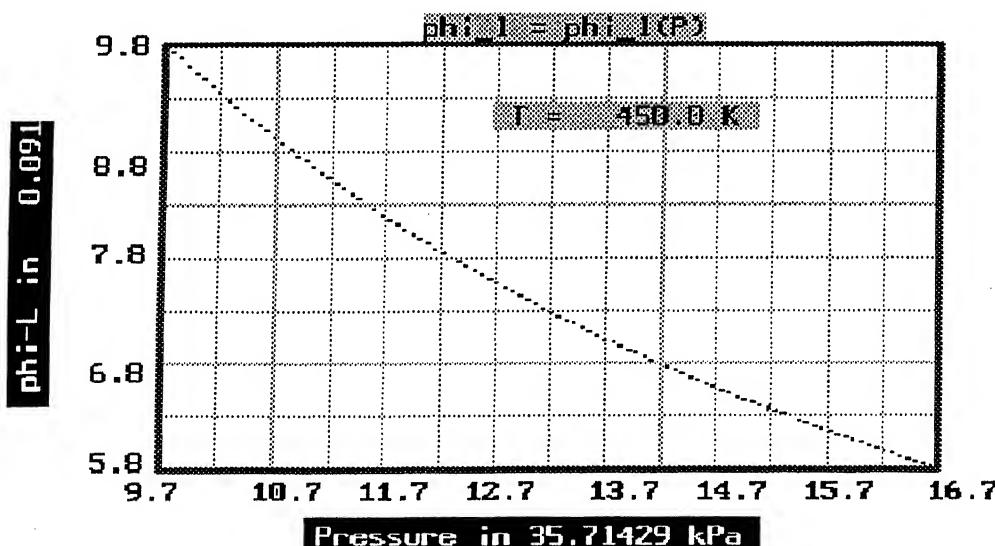
Fig. 4.4 *Fugacity coefficient of liquid vs. pressure diagram*
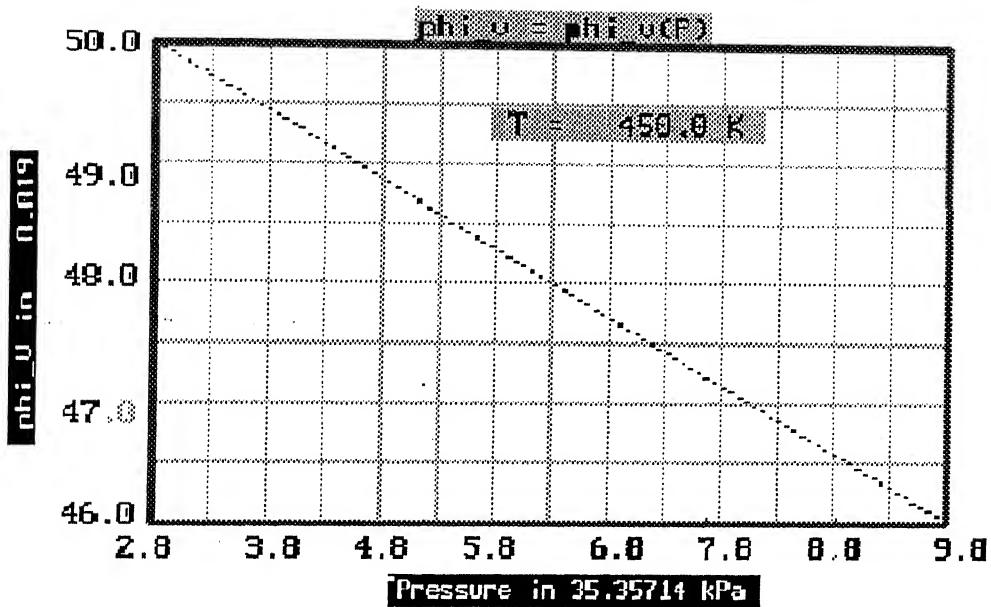
Fig. 4.5 *Fugacity coefficient of vapor vs. pressure diagram*

4.4 Sample Output For Saturation Temperature Calculation

Following is the output window, obtained by using the saturation temperature calculator to calculate Saturation temperature for *N-OCTANE* at *2.15 bar*.

Output Window

Sat. Temperature Calculations using PENG ROBINSON equation of state

Input Data:
Compound Name: N-OCTANE
Critical Temperature =   569.8 K   Critical Pressure =   24.970 BAR
Pressure   =   2.150 BAR
Acentric Factor   =   0.3980

All the Calculations were done in the following units
Temperature in Kelvin   Pressure in Pascal   Volume in m3/mol

Input Data (After Conversion)

Critical Temperature =   569.8 Kelvin   Critical Pressure =   2497000 Pascal
Pressure   =   215000 Pascal
Acentric Factor   =   0.398000

```
Iteration no:- 1
Guess Temperature =      428.6 Kelvin      Phi_L = 0.921        Phi_v = 0.922

RESULTS:

Saturation Temperature =      428.6 Kelvin


Q(Exit)              ESC(Quit to Main)     R(Run for New Data set)
```

The saturation temperature calculator can give the following *saturation temperature vs. pressure diagram*
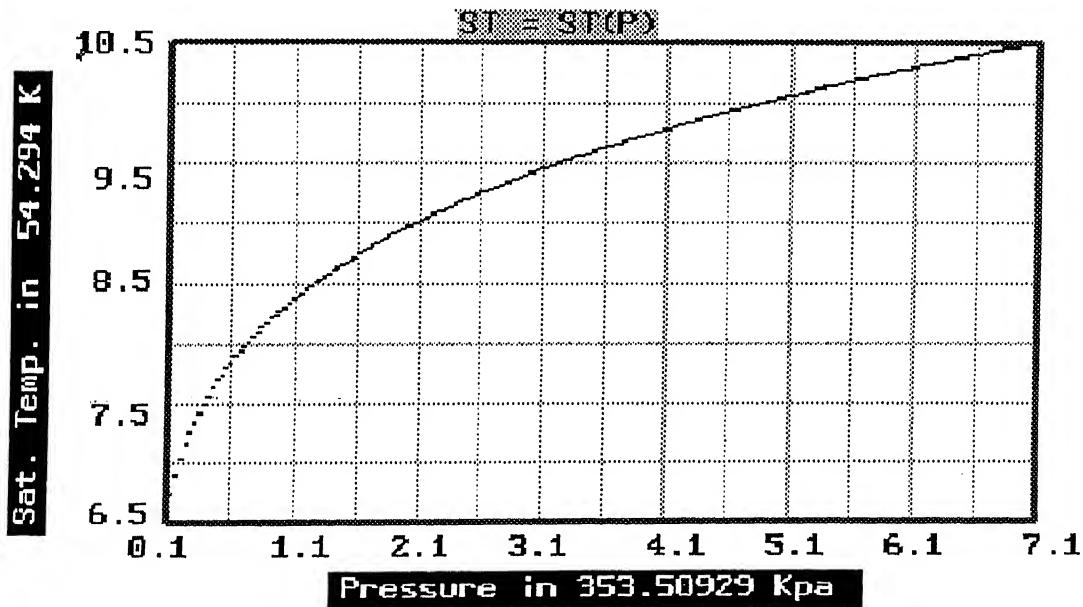

Fig. 4.6 *Saturation temperature vs. pressure diagram*

4.5 Sample Output For Saturation Pressure Calculation

Following is the output window obtained by using saturation pressure calculator for *N-OCTANE* at *450.0 Kelvin*.

Sat. Pressure Calculations using PENG ROBINSON equation of state

Input Data:
Compound Name: N-OCTANE
Critical Temperature = 569.8 K   Critical Pressure = 24.970 BAR
Temperature   = 450.0 K
Acentric Factor   = 0.3980

All the Calculations were done in the following units
Temperature in Kelvin   Pressure in Pascal   Volume in m3/mol
Input Data (After Conversion)

Critical Temperature = 569.8 Kelvin   Critical Pressure = 2497000 Pascal
Temperature   = 450.0 Kelvin
Acentric Factor   = 0.398000

Iteration no:- 1
Guess Pressure =   347.1 kPa   Phi_L = 0.889   Phi_v = 0.891
Iteration no:- 2
Guess Pressure =   346.4 kPa   Phi_L = 0.891   Phi_v = 0.891

RESULT:
Saturation Pressure =   3.5 BAR

Q(Exit)   ESC(Quit to Main)   R(Run for New Data set)

The saturation pressure calculator can give the following saturation *pressure vs. temperature diagram*.
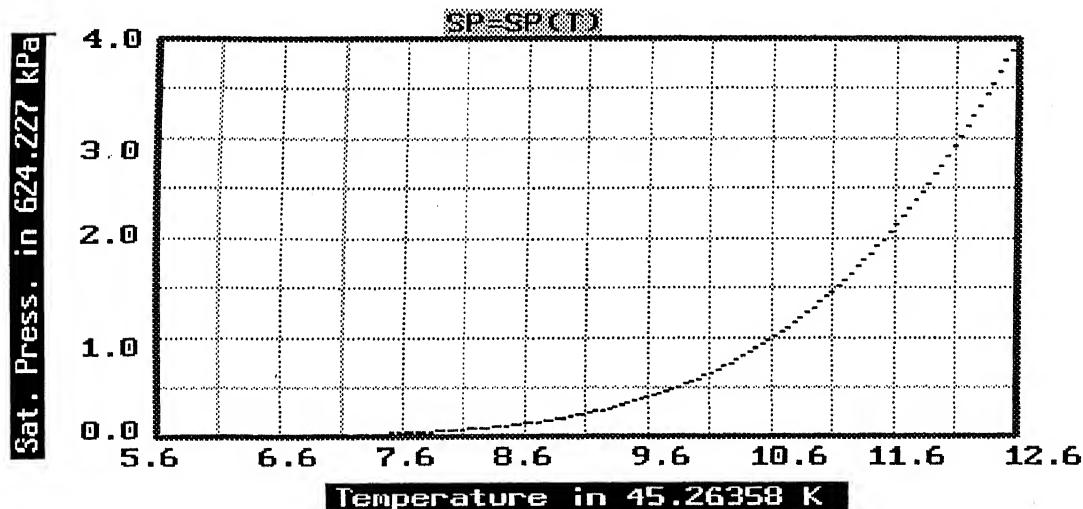
Fig. **4.**7 *Saturation pressure vs. temperature diagram*

4.6 Sample Output For Vapor Enthalpy Calculation

Following is the output window, obtained by using the Enthalpy calculator to calculate vapor enthalpy for *N-OCTANE* at *428.0 Kelvin* and *2.15 bar*.

Output Window

Vapor Enthalpy Calculations using PENG ROBINSON equation of state

Input Data:

Compound Name: N-OCTANE

Critical Temperature	= 569.8 K	Critical Pressure =	24.970 BAR
Temperature	= 428.0 K	Pressure =	2.15 BAR
Acentric Factor	= 0.3980		
Normal boiling point (NBP)	= 398.8 K		

All the Calculation were done in the following units
Temperature in Kelvin   Pressure in Pascal
Input Data (After Conversion)

Critical Temperature = 569.8 Kelvin   Critical Pressure = 2497000 Pascal

Temperature	= 428.0 Kelvin	Pressure	= 215000 Pascal
Acentric Factor	= 0.398000	NBP	= 398.8 Kelvin

H_v at NBP   = 34.864kJ/mol dh

dh1 (H_v at 298.15 K (1.976 kPa))   = 41.603 kJ/mol

dh2 (Enthalpy departure) At 298.15 K And 1.976 kPa   = 0.013 kJ/mol

dh3 (Enthalpy departure) At 427.980 K And 215.0 kPa   = -0.890 kJ/mol

dh4 (Enthalpy change due to) Change in the ideal gas state at 298.15 K and 1.976 kPa to ideal gas state at 427.980 K and 215.000 kPa   = 21.954 kJ/mol

RESULT:

ENTHALPY OF VAPOR =   65.128 kJ/mol

Q(Exit)   ESC(Quit to Main)   R(Run for New Data set)   P(Plot)

The Software can give the following Enthalpy vs. Pressure diagram for *N-OCTANE* at *T = 450 Kelvin* and in the Pressure range of *1.0 bar* to *5.0 bar*.
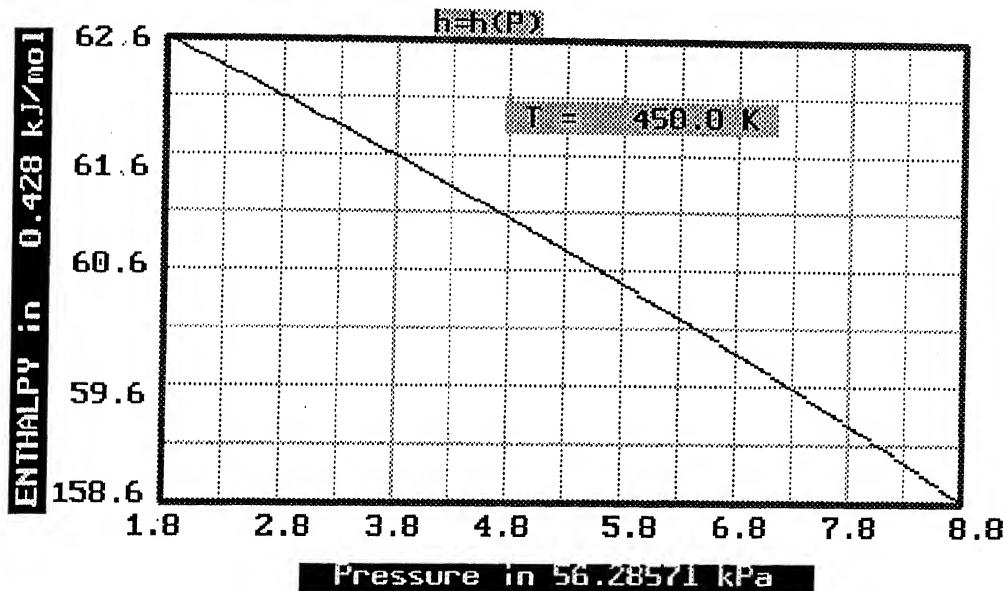

Fig. 4.8 *Enthalpy vs. Pressure Diagram*

4.7 Sample Output For Vapor Entropy Calculation

Following is the output window, obtained by using the Entropy calculator to calculate vapor enthalpy for *N-OCTANE* at *428.0 Kelvin* and *2.15 bar*.

Output Window

Vapor Entropy Calculations using PENG ROBINSON equation of state

Input Data:

Compound Name: N-OCTANE

Critical Temperature =	569.8 K	Critical Pressure =	24.970 BAR
Temperature =	428.0 K	Pressure =	2.15 BAR
Acentric Factor =	0.3980		
Normal boiling point (NBP) =	398.8 K		

All the Calculation were done in the following units
Temperature in Kelvin   Pressure in Pascal   Volume in m3/mol

The Software can give the following Entropy vs. pressure diagram for *N-OCTANE* at *T= 450 Kelvin* and in the Pressure range of *2.5 bar* to *8 bar*.
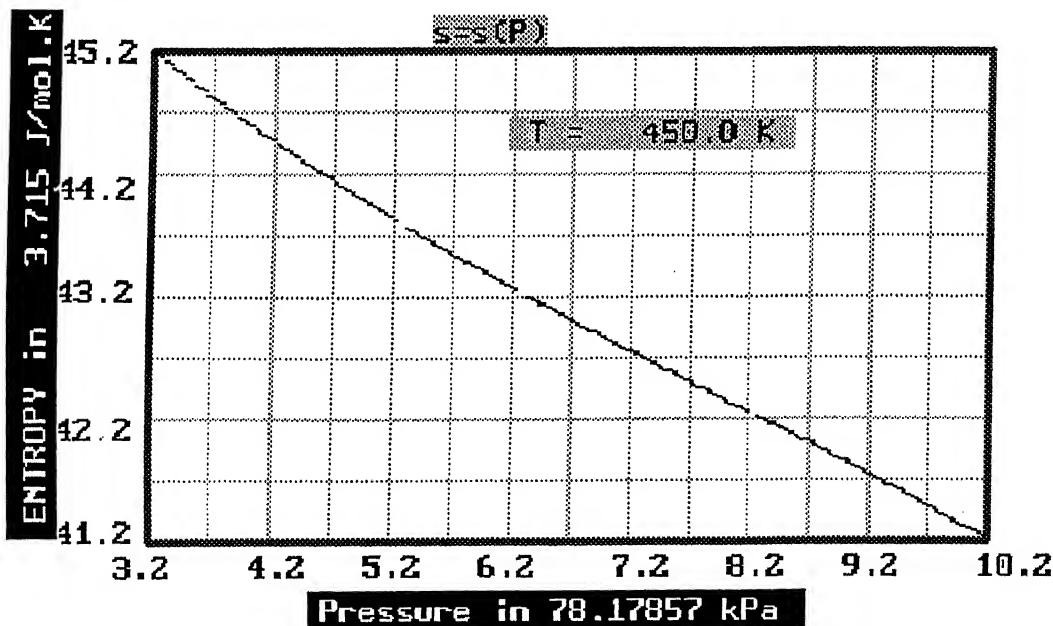

Fig. 4.9 *Entropy vs. Pressure Diagram*

4.8 Sample Output For Molar Volume Calculation of Mixture

Following is the output window, obtained by using the Software to calculate Molar Volume of *N-Octane-Toluene* mixture at *600.0 Kelvin* and *16.0 bar*. Mole fraction of *N-Octane = 0.4*

Output Window
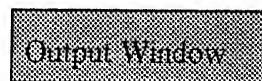
Calculation of Molar Volume of a Multi-component Mixture

Input Data:

Component Name	Tc(K)	Pc (BAR)	W	Y
N-OCTANE [1]	568.8	24.97	0.3980	0.4000
TOLUENE [2]	591.8	41.00	0.2630	0.6000

Mixture Temperature and Pressure:-

T (K) =   600.0   P (BAR) = 16.000

EOS used For Calculation is PR

For the calculations Unit of T is taken as Kelvin and Unit of P is Pascal

OUTPUT

Component No	a (Pa/mol^-2)	b (m^3/mol)
1	3.8991	1.48e-04
2	2.6715	9.34e-05
Mixture	3.1348	1.15e-04

For the Mixture parameter (a & b) calculation van der Waals mixing rule had been used.

A   = 0.201559   B = 0.036925
alpha = -0.963075   beta = 0.123620   gamma = -0.006029
p   = -0.185552   q   = -0.032512   D   = 0.000028

Vg   = 2.561e-03 cubic meter/mol

RESULT :-

Molar Volume of Vapor Mixture = 2.561e-03 m3

4.9 Sample Output For Enthalpy And Entropy Departure Calculation of Mixture

Following is the output window, obtained by using the Software to calculate enthalpy and entropy departure of *Ethanol-Methanol* mixture at *450.0 Kelvin* and *10.0 bar*. Mole fraction of *Methanol = 0.4*

Output Window

Calculation of Departure functions of a Multi-component Mixture

Input Data:

Component Name	Tc(K)	Pc (BAR)	W	Y
ETHANOL [1]	513.9	61.40	0.6640	0.6000
METHANOL [2]	512.6	80.90	0.5560	0.4000

Mixture Temperature and Pressure:-

T (K) = 450.0   P (BAR) = 10.000

EOS used For Calculation is PR

For the calculations Unit of T is taken as Kelvin and Unit of P is Pascal

OUTPUT

Component No	a (Pa/mol^-2)	b (m^3/mol)
1	1.5921	5.41e-05
2	1.1806	4.10e-05
Mixture	1.4201	4.89e-05

For the Mixture parameter (a & b) calculation van der Waals mixing rule had been used

Vapor compressibility factor (mixture) =   0.9057

RESULT :-

Enthalpy Departure of Mixture =   -1.210 kJ/mol
Entropy Departure of Mixture =   -1.927 J/mol.K

4.10 Sample Output For Fugacity Calculation of Mixture

Following is the output window, obtained by using the Software to calculate Fugacity of *Benzene-Toluene* mixture at *600.0 Kelvin* and *16.0 bar*. Mole fraction of *Toluene = 0.5.*

Output Window

Calculation of fugacityof a Multi-component Mixture				
Input Data:				
Component Name	Tc(K)	Pc (BAR)	W	Y
BENZENE [1]	562.2	48.90	0.2120	0.5000
TOLUENE [2]	591.8	41.00	0.2630	0.5000

Mixture Temperature and Pressure:-

   T (K) =   600.0   P (BAR) =   16.000

EOS used For Calculation is PR

For the calculations Unit of T is taken as Kelvin and Unit of P is Pascal

OUTPUT

Component No	a (Pa/mol^-2)	b (m^3/mol)
1	1.9508	7.44e-05
2	2.6715	9.34e-05
Mixture	2.2970	8.39e-05

For the Mixture parameter (a & b) calculation van der Waals mixing rule had been used.

A = 0.148   B = 2.690e-02   Z(Liquid) = 0.8722   Z(Vapor)= 0.8722

Vapor : PHI = 0.8833   Fugacity = 1413.265 kPa

RESULT :-

Fugacity of vapor Mixture = 14.133 BAR

Q(Exit)   ESC(Quit to Main)   R(Run for New Data set)

4.11 Sample Output For Partial Fugacity Calculation of Mixture

Following is the output window, obtained by using the Software to calculate Partial Fugacity of *Benzene-Toluene* mixture at *600.0 Kelvin* and *16.0 bar*. Mole fraction of *Benzene = 0.5*

Output Window

Calculation of Partial Fugacity a Multi-component Mixture

Input Data:

Component Name	Tc(K)	Pc (BAR)	W	Y
BENZENE [1]	562.2	48.90	0.2120	0.5000
TOLUENE [2]	591.8	41.00	0.2630	0.5000

Mixture Temperature and Pressure:-

T (K) = 600.0   P (BAR) = 16.000

EOS used For Calculation is PR
For the calculations Unit of T is taken as Kelvin and Unit of P is Pascal

OUTPUT

Component No	a (Pa/mol^-2)	b (m^3/mol)
1	1.9508	7.44e-05
2	2.6715	9.34e-05
Mixture	2.3696	8.58e-05

For the Mixture parameter (a & b) calculation van der Waals mixing rule had been used

For Vapor : A = 0.1524   B = 2.75e-02   Z = 0.8674
            phi[1] = 0.9031   f[1] =   577.983 kPa
            phi[2] = 0.8640   f[2] =   829.440 kPa

RESULT :-

Partial Fugacity of Component 1 (Vapor) =   5.780 BAR
Partial Fugacity of Component 2 (Vapor) =   8.294 BAR

4.12 Sample Output For Bubble Point Pressure Calculation

Following is the output window, obtained by using the Software to calculate Bubble Point Pressure of *Ethane-Propane* mixture at *200.0 Kelvin*. Mole fraction of *Ethane = 0.7*

Output Window

Calculation of Bubble Pressure of a Multi-component Mixture				
Input Data:				
Component Name	Tc(K)	Pc (BAR)	W	Y
ETHANE [1]	305.4	48.80	0.0990	0.7000
PROPANE [2]	369.8	42.50	0.1530	0.3000

Mixture Temperature:-   T (K) =   200.0

EOS used For Calculation is PR

For the calculations Unit of T is taken as Kelvin and Unit of P is Pascal

OUTPUT:

Calculation of bubble pressure :

Saturation Pressure of indevedual Component At   T =   200.0 K

SAT P [1] =   218 kPa
SAT P [2] =   21 kPa

Itr No	P guess	Y[1]	Y[2]	K[1]	K[2]
1	79762.046	0.79430	0.18618	2.6477	0.2660
1	79762.046	0.79430	0.18618	2.6477	0.2660
2	79762.046	0.79434	0.18614	2.6478	0.2659
3	79762.046	0.79434	0.18614	2.6478	0.2659
5	78204.982	0.80971	0.18980	2.6990	0.2711
6	78204.982	0.80977	0.18975	2.6992	0.2711
7	78204.982	0.80977	0.18975	2.6992	0.2711
9	78167.445	0.81009	0.18989	2.7003	0.2713
10	78167.445	0.81014	0.18984	2.7005	0.2712
11	78167.445	0.81014	0.18984	2.7005	0.2712
13	78166.522	0.81010	0.18989	2.7003	0.2713
14	78166.522	0.81015	0.18985	2.7005	0.2712
15	78166.522	0.81015	0.18985	2.7005	0.2712

RESULT:

Bubble Pressure of The Mixture =   0.782 BAR
Composition of the Mixture:
   Component Name   Y
         ETHANE   0.8102
         PROPANE   0.1898

4.13 Sample Output For Bubble Point Temperature Calculation

Following is the output window, obtained by using the Software to calculate Bubble Point Temperature of *Ethane-Propane* mixture at *15.0 bar*. Mole fraction of *Ethane* = 0.3

Output Window

Calculation of Bubble Temperature of a Multi-component Mixture

Input Data:

Component Name	Tc(K)	Pc (BAR)	W	Y
ETHANE [1]	305.4	48.80	0.0990	0.3000
PROPANE [2]	369.8	42.50	0.1530	0.7000

Mixture Pressure :-   P (Bar) =   15.0

EOS used For Calculation is PR
For the calculations Unit of T is taken as Kelvin and Unit of P is Pascal

OUTPUT

Calculation Of Bubble Temperature:

P   =   1500.0 kPa
SAT T [1]   =   255 Kelvin
SAT T [2]   =   317 Kelvin

Itr No	T guess	Y[1]	Y[2]	K[1]	K[2]
1	282.188	0.67414	0.38757	1.6854	0.6460
2	283.188	0.64689	0.31248	1.6172	0.5208
3	284.188	0.66530	0.31290	1.6632	0.5215
4	285.188	0.67442	0.32092	1.6861	0.5349
5	284.188	0.68334	0.32908	1.7083	0.5485
6	284.288	0.67246	0.32303	1.6811	0.5384
7	284.388	0.67448	0.32275	1.6862	0.5379
8	284.488	0.67538	0.32354	1.6884	0.5392
9	284.388	0.67626	0.32435	1.6906	0.5406

10	284.398	0.67518	0.32374	1.6879	0.5396
11	284.408	0.67537	0.32371	1.6884	0.5395
12	284.418	0.67546	0.32379	1.6887	0.5397
13	284.428	0.67555	0.32387	1.6889	0.5398
14	284.438	0.67564	0.32396	1.6891	0.5399
15	284.448	0.67573	0.32404	1.6893	0.5401
16	284.458	0.67581	0.32412	1.6895	0.5402
17	284.448	0.67590	0.32420	1.6898	0.5403
18	284.449	0.67579	0.32414	1.6895	0.5402
19	284.450	0.67581	0.32413	1.6895	0.5402
20	284.451	0.67582	0.32414	1.6896	0.5402
21	284.452	0.67583	0.32415	1.6896	0.5403
22	284.453	0.67584	0.32416	1.6896	0.5403
23	284.452	0.67585	0.32417	1.6896	0.5403
24	284.452	0.67584	0.32416	1.6896	0.5403
25	284.452	0.67584	0.32416	1.6896	0.5403

RESULT:

Tbubble (In K) =   284.45   Y[1] = 0.67584   Y[2]= 0.32416

Q(Exit)   ESC(Quit to Main)   R(Run for New Data set)

4.14 Sample Output For Dew Point Pressure Calculation

Following is the output window, obtained by using the Software to calculate Dew Point Pressure of *Ethane-Propane* mixture at *200.0 Kelvin*. Mole fraction of *Ethane = 0.3*.

Output Window

Calculation of Dew Pressure of a Multi-component Mixture				
Input Data:				
Component Name	Tc(K)	Pc (BAR)	W	Y
ETHANE [1]	305.4	48.80	0.0990	0.3000
PROPANE [2]	369.8	42.50	0.1530	0.7000

Mixture Temperature:-   T (K) =   200.0

EOS used For Calculation is PR
For the calculations Unit of T is taken as Kelvin and Unit of P is Pascal

OUTPUT:

Calculation Of Dew Pressure :

Saturation Pressure of individual Component At

T =   200.0 K

SAT P [1]   =   217761 kPa
SAT P [2]   =   20620 kPa

Itr No	Pguess(Pa)	X[1]	X[2]	K[1]	K[2]
1	79762.046	0.10233	2.44851	2.9318	0.2859
2	79762.046	0.10311	2.46667	2.9095	0.2838
3	79762.046	0.10305	2.46528	2.9112	0.2839
4	79762.046	0.10306	2.46538	2.9110	0.2839
5	79762.046	0.10306	2.46538	2.9110	0.2839
6	79762.046	0.10306	2.46538	2.9110	0.2839
7	79762.046	0.10306	2.46538	2.9110	0.2839
8	79762.046	0.10306	2.46538	2.9110	0.2839
10	31054.768	0.04414	1.04806	6.7959	0.6679
11	31054.768	0.04416	1.04821	6.7928	0.6678
12	31054.768	0.04416	1.04821	6.7929	0.6678
13	31054.768	0.04416	1.04821	6.7928	0.6678
14	31054.768	0.04416	1.04821	6.7928	0.6678
16	28428.785	0.04077	0.96203	7.3582	0.7276
17	28428.785	0.04078	0.96203	7.3570	0.7276
18	28428.785	0.04078	0.96203	7.3570	0.7276
20	28349.336	0.04067	0.95937	7.3769	0.7296
21	28349.336	0.04067	0.95937	7.3757	0.7296
22	28348.177	0.04067	0.95933	7.3771	0.7297
25	28348.177	0.04067	0.95933	7.3760	0.7297
26	28348.177	0.04067	0.95933	7.3760	0.7297

RESULT:

Dew Point Pressure of The Mixture =   0.283 BAR
Composition of the Mixture:

Component Name	X
ETHANE	0.04067
PROPANE	0.95933

4.15 Sample Output For Dew Point Temperature Calculation

Following is the output window, obtained by using the Software to calculate Dew Point Temperature of Ethane-Propane mixture at *13.0 bar*. Mole fraction of Ethane = *0.3*

Output Window

Calculation of Dew Temperature of a Multi-component Mixture

Input Data:

Component Name	Tc(K)	Pc (BAR)	W	Y
ETHANE [1]	305.4	48.80	0.0990	0.3000
PROPANE [2]	369.8	42.50	0.1530	0.7000

Mixture Pressure :-   P (Bar) =   13.0

EOS used For Calculation is PR
For the calculations Unit of T is taken as Kelvin and Unit of P is Pascal

OUTPUT:

Calculation Of Dew Temperature:

Saturation Temperature of individual Component At

P   =   1300.0 kPa

Itr No	T guess	Y[1]	Y[2]	K[1]	K[2]
1	290.000	0.14680	1.03868	2.0436	0.6739
2	300.000	0.12894	0.84933	2.3267	0.8242
3	290.000	0.14680	1.03868	2.0436	0.6739
4	291.000	0.14478	1.01718	2.0722	0.6882
5	292.000	0.14281	0.99630	2.1007	0.7026
6	293.000	0.14089	0.97602	2.1293	0.7172
7	294.000	0.13903	0.95633	2.1578	0.7320
8	295.000	0.13723	0.93720	2.1862	0.7469
9	296.000	0.13547	0.91861	2.2145	0.7620
10	297.000	0.13376	0.90054	2.2428	0.7773
11	298.000	0.13211	0.88299	2.2709	0.7928
12	299.000	0.13050	0.86592	2.2989	0.8084
13	298.000	0.13211	0.88299	2.2709	0.7928
14	298.100	0.13194	0.88126	2.2737	0.7943
15	298.200	0.13178	0.87954	2.2765	0.7959
16	298.300	0.13162	0.87782	2.2793	0.7974
17	298.400	0.13146	0.87610	2.2821	0.7990
18	298.500	0.13130	0.87439	2.2849	0.8006
19	298.600	0.13114	0.87269	2.2877	0.8021
20	298.700	0.13098	0.87099	2.2905	0.8037
21	298.800	0.13082	0.86930	2.2933	0.8052
22	298.900	0.13066	0.86761	2.2961	0.8068
23	298.800	0.13082	0.86930	2.2933	0.8052
24	298.810	0.13080	0.86913	2.2936	0.8054
25	298.800	0.13082	0.86930	2.2933	0.8052
26	298.801	0.13082	0.86928	2.2933	0.8053
27	298.802	0.13081	0.86926	2.2933	0.8053
28	298.803	0.13081	0.86925	2.2934	0.8053
29	298.804	0.13081	0.86923	2.2934	0.8053
30	298.805	0.13081	0.86921	2.2934	0.8053
31	298.806	0.13081	0.86919	2.2934	0.8053
32	298.807	0.13081	0.86918	2.2935	0.8054
33	298.806	0.13081	0.86919	2.2934	0.8053

| 34 | 298.806 | 0.13081 | 0.86919 | 2.2935 | 0.8053 |

RESULT:

Tdew (In K) =   298.81   X[1] = 0.13081   X[2]= 0.86919

4.16   Sample Output For VLE data Calculation using Excess Gibbs Free Energy Models

Following is the output window, obtained by using the Software to calculate VLE (T-x-y) data for *Ethanol-Benzene* mixture at *1.0 bar*.

Output Window

Calculation of VLE (T-x-y) data for binary mixture

Input Data:

Component Name	Tc(K)	Pc (BAR)	W
ETHANOL [1]	513.9	61.40	0.6640
BENZENE [2]	562.2	48.90	0.2120

Mixture Pressure:-   P (BAR) =   1.0

EOS used For Calculation is PR
Activity coefficient model : van Laar
For the calculations Unit of T is taken as Kelvin and Unit of P is Pascal

OUTPUT:

Pressure (At which VLE data is required) =   100.000 kPa

Component	Saturation Tempereture
1	351.49
2	352.95

T-X-Y data

No Of iteration	T (K)	X[1]	Y[1]	Gamma[1]	Gamma[2]
105	352.8	0.00000	0.00000	6.4045	1.0000
97	343.8	0.10000	0.30616	4.1788	1.0224
93	341.5	0.20000	0.39028	2.9315	1.0881
98	340.8	0.30000	0.42526	2.1919	1.1985
94	340.6	0.40000	0.44473	1.7334	1.3594
89	340.6	0.50000	0.46183	1.4403	1.5813
97	340.8	0.60000	0.48504	1.2502	1.8794
97	341.4	0.70000	0.52342	1.1277	2.2748
89	342.8	0.80000	0.59162	1.0525	2.7965
87	345.7	0.90000	0.72123	1.0123	3.4832
97	351.4	1.00000	1.00000	1.0000	4.3864

Q(Exit)   ESC(Quit to Main)   R(Run for New Data set)

4.17   Sample Output For VLE data Calculation using UNIFAC Models

Following is the output window, obtained by using the Software to calculate VLE (T-x-y) data for *Methanol-Water* mixture at *1.0 bar*.

Output Window

Calculation of VLE (T-x-y) data for binary mixture

VLE CALCULATION FOR   METHANOL [1] - WATER [2] SYSTEM

Name of the subgroups present in the binary mixture and number of times

They appear in the individual component.

Name Of Sub-Groups	METHANOL	WATER
CH3OH	1	0
H2O	0	1

Pressure =   1.0 BAR

******************** VLE-DATA ********************

T(0C)	X1	Y1	ac1	ac2
99.11	0.000	0.000	1.8431	1.0000
88.73	0.100	0.383	1.5348	1.0094
83.02	0.200	0.551	1.3439	1.0331
79.11	0.300	0.653	1.2210	1.0666
76.06	0.400	0.728	1.1396	1.1069
73.49	0.500	0.788	1.0849	1.1524
71.22	0.600	0.840	1.0483	1.2017
69.16	0.700	0.885	1.0245	1.2542
67.24	0.800	0.926	1.0099	1.3092
65.45	0.900	0.965	1.0023	1.3664
63.74	1.000	1.000	1.0000	1.4253

****

The Software can give T-x-y and x-y diagrams. The T-x-y and x-y diagrams obtained for *Methanol-Water* system at $P = 1$ bar is given in *Figs. 4.10 and 4.11*, respectively.

T-x-y PLOT

temperature (c)
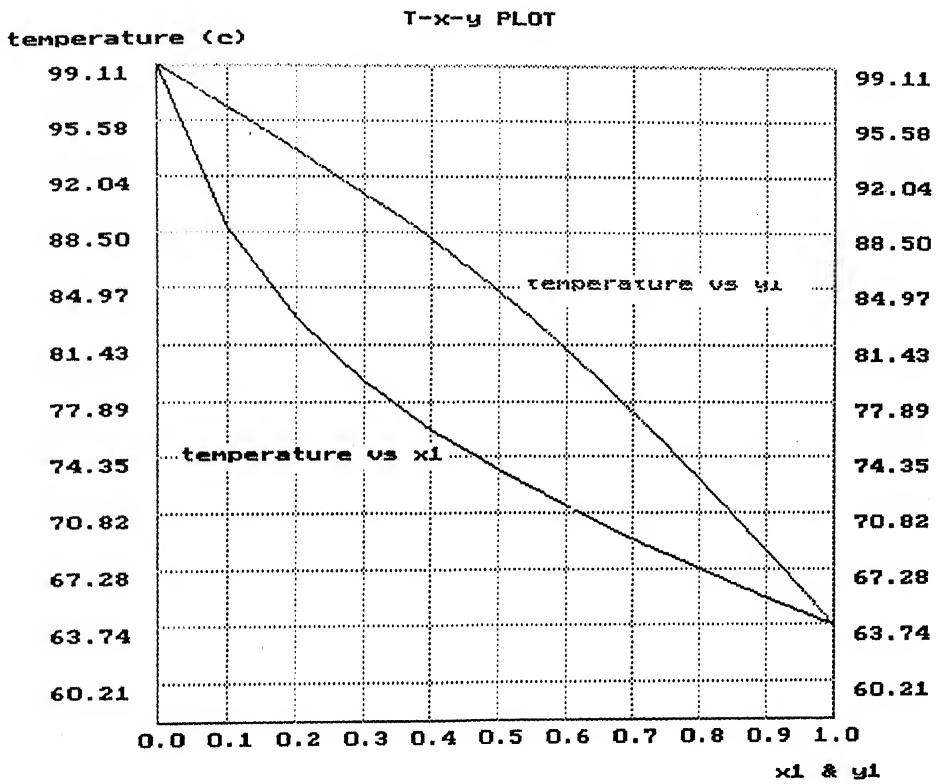
Fig. 4.10 *T-x-y diagram for Methanol [1]-Water[2] system at 1 bar.*

x-y PLOT
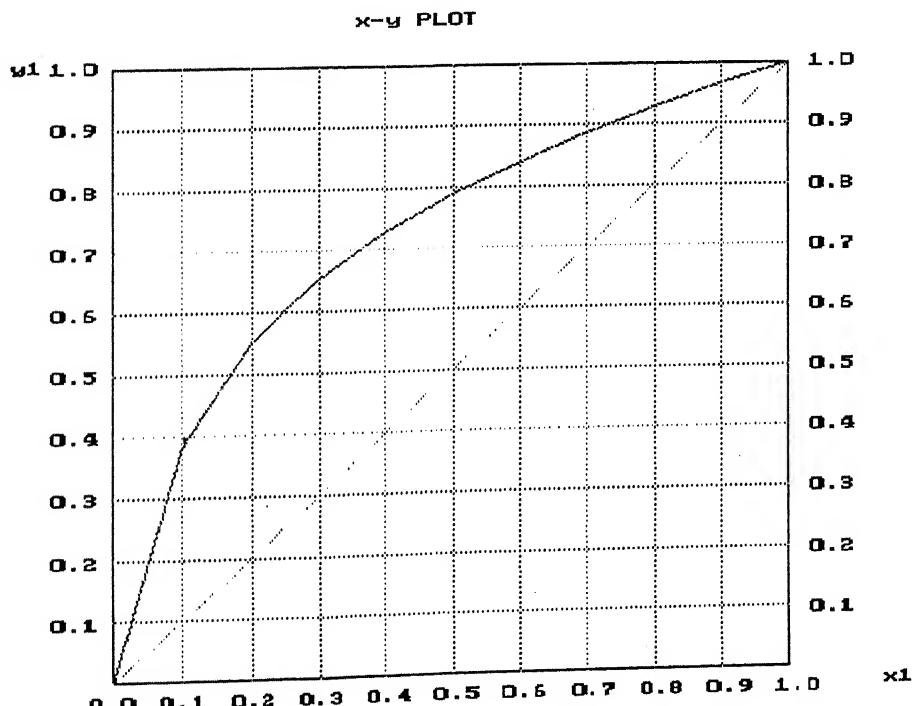
Fig. 4.11 *x-y diagram for Methanol [1]-Water[2] system at 1 bar.*

Chapter 5

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

This software is especially designed for the estimation of thermodynamic properties. It is user friendly and requires no prior knowledge of any computer language. As the software has been developed on MS-DOS operating system, it can be used only with computers, which have MS-DOS platform.

The software is a step in the direction of the development of an extensive software for chemical engineering applications. There is a need to include some more properties like viscosity, thermal conductivity, diffusion coefficients etc. For more accurate predictions newer equations of states can be used with some of the recently developed mixing rules. As for the phase equilibrium calculations liquid-liquid equilibrium, solid-liquid equilibrium etc. can be added.

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